Distillation of Palmarosa Oil in British India.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

ANNUAL REPORT

ON ESSENTIAL OILS
SYNTHETIC PERFUMES
&c.

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Contents.

List of abbreviations.

d	= specific gravity.
d_{20°	= specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d_{4^\circ}^{20^\circ}$	= specific gravity at 20°, compared with water at 4°.
α_{D20°	= optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$	= specific rotation.
n_{D20°	= index of refraction at 20°.
sol. p.	= solidifying point.
m. p.	= melting point.
b. p.	= boiling point.
n	= normal.
acet.	= acetylation.
acid v.	= acid value; ester v. = ester value; sap. v. = saponification value.
g.	= gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Commercial Notes and Scientific Information on Essential Oils.

Oil of Abies Pindrow. — Cones and young shoots of the Indian silver fir, *Abies Pindrow* (Royle) Spach[1]), yielded on steam distillation an oil, of which we received a sample some time ago. It was colourless, of agreeable balmy odour and showed the following constants: — d_{150} 0.8647, α_D — 10°59', n_{D200} 1.47328, acid v. 0.3, ester v. 6.5 = 2.3 per cent. ester (bornyl acetate), soluble with slight turbidity in 3 volumes and more of 90 per cent. alcohol; soluble in 1 vol. and more of 95 per cent. alcohol.

The tree occurs in the lower Himalaya regions, at a height of between 2400 and 3000 metres.

Oil of Aburachan. — By distillation of the leaves and twigs of *Lindera præcox*, Bl., a lauracea growing in Japan, Y. Shinosaki[2]) obtained about 0.3 per cent. of a light brown coloured oil which had a somewhat strongly camphoraceous odeur and the following characters: — d_{150} 0.9094 to 0.9178; α — 3°57' to — 5°1'; n_{D200} 1.4850 to 1.4866; acid value, 0.69 to 0.92; sap. value, 45.76 to 48.69; sap. val. after acetylation, 90.48 to 98.62. The following substances were isolated[3]): — 2 per cent. of α-pinene, 14 per cent. of camphene, 8 per cent. of cineole, 10 per cent. of an aliphatic terpene (b. p. 40 to 41° at 2 mm., d_{150} 0.8251, n_{D200} 1.4840), borneol present in the oil partly free and partly as ester, geraniol (23 per cent. with borneol), 8 per cent. of caryophyllene, 21 per cent. of d-cadinene, 5 per cent. of a sesquiterpene alcohol $C_{15}H_{26}O$, and a tertiary alcohol (b. p. 140 to 142° at 4 mm.; d_{150} 0.9740; α — 5°, n_{D200} 1.5072). From the alkaline liquor after saponification of the original oil there were isolated: — acetic acid, a decylenic acid $C_{10}H_{18}O_2$ (b. p. 106 to 107° at 1.5 mm., d_{150} 0.9339, n_{D200} 1.4552, acid value 328 to 334.9, iodine value 142.24, probably identical with citronellic acid) and a saturated weak acid of higher series and having a high boiling point.

Ajowan Oil. — Y. Murayama found in this oil a new terpene, moslene (cf. p. 51 of this *Report*).

Almond Oil, bitter. — A bitter almond oil "genuine, free from chlorine", sent us for inspection, proved an "excellent" acquisition for the buyer, as it was a crude, strongly chlorinated benzaldehyde of a reddish-brown colour (due to iron), containing about 30 per cent. of nitrobenzene.

The defects of the product were revealed at once by its constants, as it was far too heavy (d_{150} 1.1237), had too high a refraction (n_{D200} 1.54876) and did not dissolve in 50 per cent. alcohol; besides, it gave a strong chlorine reaction. It resulted on closer investigation that these irregularities were due to nitrobenzene, present in the proportion

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[1]) According to Brandis, this is only a variety of *Abies Webbiana*, Lindley. Comp. A. Engler and K. Prantl, *Die natürlichen Pflanzenfamilien* vol. II, 1, page 60. — [2]) *Journ. chem. Ind. Japan* **24** (1921), 444. According to *Journ. Soc. chem. Ind.* **40** (1921), A. 674. — [3]) Details are missing in the abstract.

indicated above. After having isolated it, it could be identified by its odour and its other properties: — d_{150} 1.2032, n_{D20} 1.55104, solidification point $+ 3.6°$.

Nitrobenzene being highly poisonous, as we have repeatedly pointed out in our *Reports*[1]), its use as an adulterant is inexcusable. We can only take it that the seller was too silly to understand the bearing of his action, otherwise he ought to have realized what ill effects the addition of nitrobenzene to a product often used in the household may have.

As E. Pinoff[2]) says, the presence of nitrobenzene in bitter almond oil can easily be proved in the following way:—10 cc. of a 40 per cent. formaldehyde solution and 20 cc. of concentrated ammonia are filled in a cylinder holding 100 cc. and which can be closed with a stopper of india-rubber. - After having shaken the mixture carefully for some time, it must be allowed to stand for five minutes. Then it is shaken vigorously with 10 cc. of the bitter almond oil and again allowed to stand. The pure bitter almond forms an emulsion with the formaldehyde-ammonia, whereas the nitro-benzene deposits as a clear liquid. The nitrobenzene is then reduced with zinc and hydrochloric acid to aniline, which can be identified by one of the well-known reactions.

We are of opinion that the usual method, according to which the benzaldehyde is bound to bisulphite, is simpler and more convenient (cf. Gildemeister and Hoffmann, *The Volatile Oils.* 2nd edition, vol. I, p. 585).

Oil of Amomis jamaicensis. — The oil of *Amomis jamaicensis* (wild pimento), the constants of which we quoted in our *Report* of 1920, p. 6 after a communication in the *Bulletin of the Imperial Institute*, London, has been further investigated by O. D. Roberts[3]). After removing the free acids (0.2 per cent. acetic and caproic acids), an aldehyde (0.1 per cent.) and a phenol (0.1 per cent., *not* eugenol) the oil was hydrolysed with boiling alcoholic potassium hydroxide and the oil separating after addition of water and extracting with ether was submitted to fractional distillation at 14 mm. pressure, which gave the following fractions: — 1. B. p. 75 to 80° (175 to 190° at ordinary pressure), 32 per cent. of the original oil; 2. b. p. 80 to 95° (190 to 205°, ord. pr.), 42 per cent.; 3. b. p. 95 to 110° (205 to 220°, ord. pr.), 4 per cent.; 4. b. p. 110 to 125° (220 to 235° ord. pr.), 6 per cent.; residue 16 per cent. of the original oil. Fraction 1 contained 47 per cent. cineole = 15 per cent. of the original oil (resorcinol method and iodole addition compound), α-phellandrene (nitrite, m. p. 112 to 113°), and dipentene (tetrabromide, m. p. 124°). The principal part of fraction 2 had the constants: — b. p. 197 to 198°, d_{150}^{150} 0.8693, α_D —3°39', n_{D20} 1.4655 and was identical with l-linalool (oxidation to citral; α-citryl-β-naphthocinchoninic acid, m. p. 200°). In fraction 4 geraniol was proved to be present (diphenylurethane, m. p. 80 to 81°). The residue boiling above 235° was heated on the water bath under reduced pressure for some weeks with sodium. There was thus obtained by distillation under 15 mm. pressure a colourless oil, with a slight balsamic odour, b. p. 245 to 290° (uncorr.), d_{150}^{150} 0.9320, which was still slowly attacked by sodium.

The author summarizes his investigation as follows: — The oil of *Amomis jamaicensis* contains about 17 per cent. of terpenes (α-phellandrene and dipentene), 15 per cent. of cineole, 38.3 per cent. of alcohols (chiefly l-linalool with some geraniol), 1.5 per cent. of ester (linalyl acetate), each 0.1 per cent. of phenols and aldehydes, both undetermined, 0.2 per cent. of acetic and caproic acids, and 27.8 per cent. residue probably containing sesquiterpenes.

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[1]) Cf. for instance *Report* 1918, 5. — [2]) *Pharm. Zentralh.* 62 (1921), 610. — [3]) *Journ. Soc. chem. Ind.* 40 (1921), T. 95.

Oil of Andropogon Iwarancusa.— J. L. Simonsen[1]) investigated the oil of *Andropogon Iwarancusa,* Jones, a graminea occurring in the Himalayas and the outer hill zone from Kashmir to Assam and ascending to 8000 ft. and above, also in the plains from North West Himalaya to Bombay Presidency. The pale yellow oil, which had been obtained in a 1 per cent. yield from the grass, possessed a marked smell of peppermint and had the following constants:— $d_{30°}^{30°}$ 0.9203, $[\alpha]_{D30°}$ +51.68°, $n_{D30°}$ 1.481, acid v. 0.7, sap. v. 12.0, sap. v. after acet. 47.4, percentage of ketone, by absorption with neutral sodium sulphite solution, 77 per cent. On distilling and refractionating the oil under diminished pressure (200 mm.), the following fractions were obtained:— 1) 115 to 130° (14.6 per cent.), 2) 130 to 174 (1.6 per cent.), 3) 174 to 185° (70 per cent.), 4) 185 to 205° (12 per cent.). The first fraction consisted essentially of a hydrocarbon, b. p. 101° (100 mm.), 163 to 164° (698 mm.), $d_{30°}^{30°}$ 0.8565, $[\alpha]_{D30°}$ +54.82°, $n_{D30°}$ 1.474, smelling pleasantly reminiscent of cymene. When dissolved in acetic anhydride and treated with a drop of sulphuric acid, a transient purple coloration appeared, which rapidly passed into a deep brown. When the hydrocarbon was treated with hydrogen chloride in ethereal solution, an oil resulted which was probably a monohydrochloride; with hydrogen bromide in acetic acid solution a viscous oil was obtained, which was evidently a dihydrobromide $C_{10}H_{18}Br_2$. The hydrogen iodide derivative was very unstable, and decomposed even when kept at 0°. Fraction 2) consisted apparently mainly of a mixture of d-Δ^1-p-menthenone-3 and the hydrocarbon. Fraction 3) ($d_{30°}^{30°}$ 0.9321, $[\alpha]_{D30°}$ +36.76°, $n_{D30°}$ 1.481) consisted, by 98 per cent., of d-Δ^1-p-menthenone and was purified by solution in sodium sulphite solution and reprecipitation (and racemisation, comp. Read and Smith, p. 34 of this *Report*) by alkali, when it showed the following constants:— b. p. 180 to 181° (200 mm.), 230 to 231° (697 mm.), $d_{30°}^{30°}$ 0.9307, $[\alpha]_{D30°}$ +7.92°, $n_{D30°}$ 1.481. Fraction 4) still contained a considerable quantity of the ketone. The identity of the racemic ketone with dl-Δ^1-p-menthenone-3 = piperitone (comp. p. 149 of this *Report*) is proved, according to Simonsen, by the formation of the benzylidene derivative (m. p. 61°) and the hydroxylamino-oxime (m. p. 170 to 171°), furthermore by oxidation of the ketone, by ferric chloride, to thymol and by the reduction to menthol. Besides, the author prepared:— the α-semicarbazone (m. p. 225 to 227°), the β-semicarbazone (m. p. 174 to 176°), an optically active β-semicarbazone (m. p. 193 to 194°), the oxime (m. p. 117 to 118°), and proved thus the identity of his ketone with the Δ^1-menthenone-3 obtained by Wallach and others[2]). The discrepancies observed in the constants as compared with the values found by former authors (α-semicarbazone, m. p. 224 to 226°, β-semicarbazone, m. p. 171 to 172°, oxime, m. p. 107 to 109°) are explained by Simonsen by assuming that the compounds obtained formerly had not been quite pure and free from isomerides.

On oxidising the ketone with potassium permanganate solution, at 0°, l, γ-acetyl-α-isopropylbutyric acid was obtained; b. p. 195 to 200° (48 mm.).

Thus the oil of *Andropogon Iwarancusa* consists up to 80 per cent. of d-Δ^1-menthenone-3 and of a hydrocarbon of unknown constitution.

Angelica Oil.— Last autumn, it is true, the Thuringian plantations supplied abundant quantites of raw material, but the prices remained high, as there was a vivid demand, owing to the completely exhausted stocks of oil. Although we had secured considerable lots, our production was scarcely large enough to come up to the requirements from all quarters, so that we were almost sold out at the beginning of the present year. The prospects are not very favourable, as there are only few

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[1]) *Journ. chem. Soc.* 119 (1921), 1644. — [2]) Comp. *Reports* October 1910, 99; 1916, 18.

fresh plantations in Thuringia which, besides, will yield material for distillation only in 1923. The shortage of oil will therefore continue.

From fresh angelica roots, Roure-Bertrand Fils[1]) obtained by water-and-steam distillation 0.4 per cent. of a golden-yellow oil with the following qualities: — $d_{17.50}$ 0.8887, d_{150} 0.8907 (corr.), α_{180} +6°42′, acid v. 7.20, ester v. 45.07, sap. v. 52.27; soluble in 2 and more vols. of 90 per cent. alcohol. The odour of the oil was inferior to that obtained from dried roots. The low optical rotation and the high acid and ester values differed from the normal figures. — The oil extracted from aqueous distillate by means of light petroleum showed an odour less intense than that of the principal oil, it was dark red and had the constants: — acid v. 20.53, sap. v. 134.40; soluble in 90 per cent. alcohol with slight opalescence, entirely soluble in 95 per cent. alcohol.

Apple Oil. — Basing on their investigations on the composition of the odorous principle of ripe apples[2]) F. B. Power and V. K. Chesnut[3]) publish particulars of a U. S. Pat. (No. 1366541) for synthetic apple oil. This oil is composed of the *iso*amyl esters of formic, acetic, caproic and caprylic acids, together with acetaldehyde, or of these components without the *iso*amyl caproate. According to the abstract available, the mixture, which may be employed either in the concentrated state or in alcoholic solution, consists of: — *iso*amyl formiate 10 pts., *iso*amyl acetate 10 pts., *iso*amyl n-caproate 5 pts., *iso*amyl caprylate 1 pt., acetaldehyde 2 pts.

As to the paper published by Kodama (comp. p. 154 of this *Report*) and bearing the title: "On the odour of apples; ethereal oils obtained from leucic acid", F. B. Power and V. K. Chesnut[4]) remark that, according to their investigations, the esters prepared by Kodama do not occur in apples[5]). Hence, the title given by Kodama to his communication is not only misleading but entirely unwarranted.

Atlas Cedar Tar. — In the well-wooded region of Azrou, south-east of Meknes, the natives prepare through incomplete combustion of the roots of *Cedrus atlantica*, Manetti, a tar which was recently investigated by R. Massy[6]). The author states that a long pit, lined with clay and situated on an incline, serves for the purpose. The lowest part of it is connected through a narrow pipe with a hole, into which the distillation products flow. After having filled the pit with the pieces of wood from the roots, the largest at the bottom, and covered with branches of the tree and sand, the wood is lit from the side opposite the escape-pipe, left open for the purpose. The slower the combustion, the better the yield. After about twelve hours, the distillate collected in the hole is taken out and filled into a hanging skin bag, in which the tar separates from the water, this then being removed. The distillation is completed after another 24 hours, when the new distillate is treated in the same way. 241 kilos of cedar wood thus yielded 17.78 kilos (7.4 per cent.) of crude tar, corresponding to 4 per cent. of filtered tar. The final product had the following properties: — d_{200} 0.981 to 0.985; on being distilled under ordinary pressure between 150 and 300°, 71 per cent. of a dextrorotatory body passed over. The products carried over by steam are dextrorotatory. Less than 5 c.c. of N/soda lye suffice to neutralize the acid contained in

[1]) *Bull. Roure-Bertrand Fils*, October 1921, 33. — [2]) Comp. *Bericht* (German) 1921, 7; also the work of Thomae, *Reports* October 1911, 21; April 1913, 28. — [3]) *Perfum. Record* 12 (1921), 123. — [4]) *Journ. Americ. chem. Soc.* 43 (1921), 1741. — [5]) Comp. *Bericht* (German) 1921, 7. — [6]) *Journ. de Pharm. et Chim.* VII. 24 (1921), 264.

100 c. c. of tar, which acid is soluble in cold water. Every 100 c. c. of tar contain 10.3 to 12.8 grams of constituents soluble in 5 per cent. soda lye, precipitable by means of hydrochloric acid and soluble again in ether.

Bay Oil. — According to Robson[1]), Curator, Montserrat, the results from the bay tree experiment plot in 1919 were more favourable than ever. Although fifty-two distillations were made of leaves reaped from the plot, it was not possible to deal in the still at the Botanic Station with the total quantity reaped, and therefore 1255 lbs. were sold to a distiller at the close of the year. Several thousand pounds of leaves were left unreaped on account of the unability to deal with them. Once the trees are sufficiently developed actually to cover the ground occupied, less and less cultivation is required. The average yield of oil per 100 lbs. of green leaves in this season on the whole of the distillations was 17.3 ozs., compared with an average of 18.6 in the previous year. The best average results have been obtained between January and July. This, however, may be entirely due to the effect of the usual dry weather at this time of the year, and to the leaves having a reduced water content as the result of evaporation. On the question of the quality of the oil as indicated by the specific gravity and the phenol content, the best results in 1917 were obtained in March, April and May; in 1918, in June and July; and in 1919, in the month of October. A trial was made with old leaves, many of which had been on the trees for at least two years, but the result was disappointing in every respect.

A bay oil from Mexico may be mentioned here just for the sake of its particular origin. It was only slightly inferior in quality to good West Indian oils: — d_{15^0} 0.9658, $\alpha_D - 1^0 50'$, n_{D20^0} 1.50891, soluble in 0.5 vol. of 80 per cent. alcohol. A further addition of alcohol caused opalescence. The eugenol content, determined with the aid of 3 per cent. soda lye, was 55 per cent.

Birch Tar Oil. — Our repeated endeavours to procure at least small quantities of this product, which originates exclusively from Russia, having failed, it was impossible so far to satisfy the demand for this oil, so indispensible for the manufacture of a good Russian leather perfume. It is quite understandable, however, that the disastrous economic conditions of that country imply that all attention be directed for the time being to more important products, so that the users of the article must wait patiently still longer.

J. Pritzker and R. Jungkunz[2]) publish an article on the investigation of the oils of birch tar and other wood tars. From the review of previous publications, given by the authors, it results that the indications regarding the definition of birch tar and the parts of the tree used for its manufacture differ considerably. Some say, it is obtained from the bark; others, from bark and twigs, or from the roots, from the wood, etc. The authors failed in their attempts to obtain absolutely pure birch tar. The results of their investigations show great differences, especially with regard to the indices of refraction, which vary between 50.9 and above 100. However, they afford some general information, which may be useful for further tests of birch tar oils.

A product styled „Russian leather fat" (birch tar oil), repeatedly offered in Switzerland, resulted to be a strongly rancid fat, perfumed with some artificial aromatic. Two other birch tar oils were strongly adulterated (more than 50 per cent.) with mineral

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[1]) *Chemist and Druggist* **95** (1921), 350. — [2]) *Schweiz. Wochenschrift f. Chem. u. Pharm.* **59** (1921), 146, 162.

oils. A pre-war sample of birch tar oil, taken from our research laboratories' collection, showed an extraordinarily high content of unsaponifiable constituents, which was not due to any admixture of mineral oils. A test for resinous matter gave a negative result. Another birch tar oil, surely originating from the neighbourhood of Minsk, had the characteristic Russian leather smell and contained 55 per cent. of resin, as well as 32 per cent. of unsaponifiable matter of pitchlike character.

The author states that Zeiss' butter refractometer answered very well for the determination of refraction, whereas Storch's reaction (anhydrous acetic acid and sulphuric acid) was a useful test for resinous bodies. As tars from conifers consist almost exclusively of resin, but tars from deciduous trees contain very little resin, the indices of refraction of the various tars and of their distillation products afford a means of distinguishing them, especially if the saponification value, the acid value and the amount of unsaponifiable products are likewise taken into consideration.

Oil of Boldo Leaves. — Roure-Bertrand Fils[1]) obtained from the leaves of the boldo tree, *Peumus Boldus*, Mol., *Monimiaceæ*, by distillation with steam, a golden-yellow oil[2]), the odour of which resembled that of cineole and chenopodium oil. It showed the following constants: — d_{170} 0.9318, d_{150} 0.9334, α_{110} — 0° 14', acid v. 1.87, ester v. 13.0, cineol content 30 per cent. Besides, the sample investigated contained 10 per cent. of constituents soluble in 3 per cent. soda lye. After having been freed from the alkali and dissolved in alcohol, they gave a greenish yellow colour reaction with ferric chloride. The acetylated oil showed α_{D150} + 1°, ester v. 70.93.

On shaking the distillation water of 40 kilograms of leaves with light petroleum, 20 grams of an oil were obtained which was much darker and smelled quite different from the product obtained direct. It had the following properties: — d_{150} 0.9323, α + 0°, acid v. 3.73, ester v. 22.40, ester v. after acetylation 142.18. The authors think that the high acetylation value is due to decomposition products of the ascaridole. The acetylated oil smelled distinctly of terpinyl acetate. With the aid of 5 per cent. soda solution, 15 per cent. phenols were separated from the oil, they smelled of carvacrol and coloured green with ferric chloride.

Oil of Boronia pinnata. — The oil obtained by steam distillation from *Boronia pinnata*, Sm., a *Rutacea* occurring in Australia, showed according to Smith[3]) the following properties: — amber-yellow colour, aromatic odour like geranyl acetate and geraniol, d_{150} 1.0197, α + 3.8°, n_{D200} 1.5125, saponification v. 20.2, id. after acetylation 36,9, content of geranyl acetate 6.4 per cent. The oil contained also free geraniol, geranyl butyrate, trimethyl gallic acid and 70 per cent. elemicin $C_{12}H_{16}O_3$[4]).

Oil of Buchu Leaves. — As per the annual statement of trade and shipping of the Union of South Africa[5]), the exports of buchu leaves were as follows: —

1919	149166 lbs. to the value of 37130 £
1920	139149 „ „ „ „ „ 67243 „ .

The average annual export for the five years 1910 to 1914 was 204271 lbs., valued at 30394 £, while the average for the five years 1915 to 1919 was 130161 lbs., valued

[1]) *Bull. Roure-Bertrand Fils*, April 1921, 14. — [2]) Nothing is said about the yield. — [3]) *Proceed. Royal Soc. Victoria N. S.* 1 (1919), 32. According to *Bull. Roure-Bertrand Fils*, April 1921, 113. — [4]) There are no other details. — [5]) *Chemist and Druggist* 94 (1921), 745.

at 23937 £. The world's demand for both the buchu leaves and oil is rapidly increasing, and the future prospects of buchu as a field crop are good, so that increased interest is being taken in the cultivation of the plant.

Cade Oil. — There are two methods[1]) of preparing cade oil; *viz.*, the *"destillatio per descensum"* for small amounts and the *"combustion en milieu confiné"* for large quantities. As A. Juillet[2]) says, Planchon described in 1911 a new apparatus, which is more easily worked and is said to give better yields than the old furnaces. Planchon avails himself of the *"destillatio per descensum"*, which he has improved somewhat and carries out on a larger scale. A jug-like container of a capacity of 1 cbm., being 1.70 m. high and having a diameter of 0.5 m. in the centre, is used for the dry distillation of the wood. This furnace, the walls of which are made of bricks and are about 15 cm. thick, stands on an inclined stone plate, has a small opening on top (diameter 20 to 25 cm.?) and another at the bottom, which is superficially closed during the distillation with a flat stone. A strong hemispherical brick-work, which has several apertures at the bottom, surrounds the furnace in such a way that the distance between the two walls (45 cm. at the bottom, decreases gradually higher up, but the opening on top is left free. Through the latter the furnace is filled with pieces of wood of *Juniperus Oxycedrus*, 6 to 25 cm. long. Then the opening is shut by means of a flat stone and earth and a fire is made in the space between the two walls and kept up for twelve hours. After this time, the walls are so hot that the distillation continues for another 6 to 8 hours. The distillation products, flowing out of the lower opening, are collected in a large vessel and treated in the well-known way[3]).

With this furnace, used in the departments of Gard and Hérault (Sommières), about 4 to 6 kilos of cade oil can be obtained in one distillation from 250 kilos of wood. This yield seems susceptible of an increase.

The author remarks that there would now be again more demand for genuine cade oil, as there was a method of distinguishing between the pure product and faked stuff[4]). The cheap adulterated products form Norway and Asia Minor have no therapeutic value at all, whereas the genuine article is an excellent remedy against skin diseases, especially for animals.

Mr. B. Ménaché[5]), of Barcelona, estimates that 80 tons of pure cade oil are produced yearly in Spain, 30 tons of which are consumed locally, and the balance of about 50 tons are available for export. The cade tree, *Juniperus Oxycedrus*, L., grows in abundance only in the hilly and rocky districts, this is to say far away from railways and even carriage-roads. To give an idea of the distance between "civilization" and the cade growing country, Mr. Ménaché mentions that it takes a two hours' carriage journey, followed by a six hours' ride on horseback, to go from the railway station to his nearest stills, fitted up in 1920 according to the French system[6]), but with iron stills.

Although the best oil is obtained from the roots alone, generally roots and stems e distilled together. Such genuine oils, obtained by Mr. Ménaché in various places, ᵈ the following properties: — d_{150} 0.955 to 0.990, completely soluble in ether, soluble ith slight opalescence in 20 vols. of 90 per cent. alcohol, colour like burnt sugar.

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[1]) Comp. *Report* November 1908, 24. — [2]) *Parfum. moderne* 13 (1920), 165. — [3]) Comp. *Report* November 8, 25. — [4]) It is to be regretted that the author does not give any details. We would refer to Huerre's vestigations, which might perhaps be useful for the test of cade oil (*Report* 1919, 9). — [5]) *Perfum. Record* (1921), 149. — [6]) *Berl. Berichte* 47 (1914), 2258.

Years ago, H. Huerre[1]) showed that direct distillation of the wood of *Juniperus Oxycedrus* yielded 8.11 per cent. of cade oil, or, if the essential oil had previously been removed, only 5.62 per cent. of distillate. In a new treatise, Huerre[2]) examines the relations between the content of essential oil in the wood and the yield of cade oil. The raw material for his experiments was coarsely powdered wood of *Juniperus Oxycedrus,* from which the essential oil had been drawn by steam distillation and the resin extracted by means of ether and acetic ether. This material was subjected to dry distillation, partly with an admixture of 3 to 5 per cent. of the essential oil of *Juniperus Oxycedrus,* partly without. During the distillation, which took four hours, the temperature rose after less than two hours from 98 to 203°, then sank to 180° and remained constant till the end. In the interior of the wood, it reached 402° and remained constant, after two hours, between 380 and 385°. Six different experiments, carried out in this way, had the following results: — 1) In the presence of 5 per cent. essential oil: 9 per cent. oil, lighter than water, 32 per cent. water, 9 per cent. tar, 37.5 per cent. charcoal. 2) Without any addition: 0 per cent. light oil, 36 per cent. water, 2.5 per cent. tar, 37.5 per cent. charcoal.

Huerre concludes from these results that the essential oil of *Juniperus Oxycedrus* passes over completely with the cade oil and serves as a solvent for the heavy tar. The author's other observation that during the distillation cadinene is transformed only to the extent of 20 to 25 per cent. is not new, for F. W. Semmler and W. Jakubowicz[3]) have shown already that a large proportion of cadinene remains unaltered at a temperature of 330°.

It had been taken for granted that the brown colouring with copper acetate and light petroleum sufficed to characterize genuine cade oil. According to H. Huerre[4]), "cade oil for veterinary use", the origin of which is unknown, gives the identical reaction, the same as the essential oils obtained by dry distillation from other conifers, with the exception of *Pinus maritima* (Poir. or Mill.?). The oils of *Juniperus Virginiana,* L., and *Cedrus Libani,* Barrel., the same as cade oil, yield after treatment with dilute soda lye on distillation under normal pressure 55.5 and 62.5 per cent., respectively, of fractions passing over between 250 and 300°, in addition to a distillation residue of 7.5 and 10 per cent., respectively. The author intends to publish shortly an article on a new reaction of cade oil (by means of the dihydrochloride of cadinene).

A treatise by R. Massy[5]) deals with the tars obtained from African conifers as substitutes for cade oil. The author describes the botanical origin of these products (*Thuja, Juniperus* and *Cedrus* species), the methods of production and the principal properties of the tars.

Cajuput Oil. — The export figures for the provinces of Ambon and Celebes, including those of the island of Boeroe, are now available up to 1918. The direct exports, chiefly via Singapore, were: —

	1916	1917	1918
to British India and China	84000 kilos	77000 kilos	33000 kilos
besides, to Java	71000 „	83000 „	79000 „ .

Java re-exports a considerable part of its imports. The Javanese use the oil not only as an embrocation for contusions, excoriations, wounds and head-aches, but also against bugs.

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[1]) *Bull. Sciences pharmacol.* 28 (1921), 299. As per *Chem. Zentralbl.* 1921, IV. 812. — [2]) *Bull. des Trav. de la Soc. de Pharm. de Bordeaux,* June 1921. According to a reprint kindly sent us. — [3]) *Berl. Ber.* 47 (1914), 2077. *Report* April 1915, 85. — [4]) Comp. above. — [5]) Comp. *Report* 1919, 8.

The chief shipping place is Macassar, the official statistics of which port show the considerable fluctuations of the last years.

The shipments were:—

1914	381	cases or baskets	1918	624	cases or baskets
1915	4481	„ „ „	1919	2802	„ „ „
1916	3359	„ „ „	1920	1324	„ „ „
1917	1546	„ „ „	1921	1805	„ „ „ .

The investigation of a cajuput oil, sent us for the purpose, showed once again very clearly that the constants alone are not always a safe criterion for the quality of the oil. Specific gravity, rotatory power and solubility were altogether normal ($d_{15°}$ 0.9209, $\alpha_D — 0°36'$, soluble in 1 vol. and more of 80 per cent. alcohol) but the odour proved that the product consisted chiefly of a camphor oil fraction containing cineole, which had been adjusted to the constants of cajuput oil. The camphor-like odour was so unmistakable that a special chemical proof was not required.

A great lack of moral sense is required to place such stuff on the market and this case shows again how necessary it is to buy only from reliable firms.

Camphor Oil. — The exports of camphor oil from Japan, after a considerable rise in 1920, decreased very much in 1921. In the years from 1919 to 1921, they were as follows[1]: —

1919	. . . .	10306 piculs to the value of 333785 yen
1920	. . . .	23424 „ „ „ „ „ 841508 „
1921	. . . .	8056 „ „ „ „ „ 167256 „ .

An extensive article in the *Bulletin of the Imperial Institute*[2] on the "Present position of the camphor industry" deals with the history and the prospects of camphor production in China, Japan and Formosa. In addition the cultivation of the camphor tree in Italy, Algeria, South Africa, West Usambara, America, the West Indies, Buenos Aires, Burma, the Nilgiris, the Straits Settlements, the Federated Malay States, Queensland, Ceylon, Madagascar, Mauritius and the Canaries is discussed with more or less details. As our readers will already be fairly well acquainted with the subject, we only extract from the article what can serve as a completion of our previous communications.

Formerly, camphor came to Europe almost entirely in the crude state, from China, Formosa, or Japan, the process of refining being a Dutch secret at the close of the seventeenth century and afterwards a Venetian monopoly, but more recently carried out in England, Hamburg, Paris, New York and Philadelphia, as well as in Japan. — 1912 it was estimated that 70 per cent. of the world's consumption of camphor[3] — then 11000000 lbs. — was used for the manufacture of celluloid. Since then, the rapid increase of the cinematograph industry has led to a greatly enlarged demand for it as a material for the manufacture of films and similar products, such as xylonite. The total amount of camphor taken by Europe and the United States in 1914 is said to have been 12000000 lbs.

The Chinese export of camphor in 1891 (before the cession of Formosa) was 17000 piculs (over 2250000 lbs.), and, according to a Chinese authority, the province of Fukien alone had in 1905 more camphor trees than Formosa. Between 1903 and 1907, the province was overrun by Japanese employés and, according to the Chinese

[1] *Chemist and Druggist* 96 (1922), 468. — [2] *Bull. Imp. Inst.* 18 (1920), 524. — [3] It is supposed that in the ten first years of this century 7 to 10 million lbs. were consumed annually, on an average, in the whole world, as compared with 17 million lbs. in 1916, 12 million lbs. in 1917 and 10 million lbs. in 1913.

authority already quoted, the Japanese saw that it was only by rapidly destroying the industry in Fukien that they could create a monopoly for themselves. The export of camphor from Foochow rose from 264 cwts. in 1902 to 13535 cwts. (1516600 lbs.) in 1906. As all the available trees were cut down and no planting took place, the industry rapidly declined afterwards, as shown by the following table.

Total Chinese Exports of Camphor in Pounds: —

1907	. .	3433937 lbs.	1912	. .	331000 lbs.	1915	. .	181735 lbs.
1908	. .	1742933 „	1913	. .	248700 „	1916	. .	316933 „
1911	. .	448133 „	1914	. .	241333 „	1917	. .	472933 „ .

The revival under the stimulus of rising prices which is here shown after 1915 came mainly from the province of Kiangsi, in which there are stated to be camphor forests and some undeveloped territory, especially in the south. In 1919 Kiukiang alone produced 332266 lbs., and the following statistics[1] show how considerably the Chinese camphor export has revived again since 1919.

Exports of Camphor from China: —

1916	. . . .	2377	piculs	(316850 lbs.)	181673	tæls
1917	. . . .	3547	„	(472800 „)	261918	„
1918	. . . .	5742	„	(765400 „)	428074	„
1919	. . . .	23093	„	(3078300 „)	1595313	„
1920	. . . .	29997	„	(3998600 „)	2840043	„ .

American buyers are looking to China for an immediate addition to the supply, as in the Shan States of South-West Yunnan there are stated to be an immense number of camphor trees only awaiting transport facilities for their exploitation. The Chinese authority already quoted recommends that an American Syndicate should start operations in South Hunan and South Kiangsi, establishing distilleries on modern lines, cutting in a conservative manner, and encouraging planting by demonstration plantations, lectures, pamphlets, and the free distribution of seed and seedlings, and should afterwards extend their action into Kweichow, Kwangtung and Kwangsi.

In Japan, the export, which had been over 6577000 lbs. in 1889 and about 5860000 lbs. in 1891, had fallen to 2961000 lbs. in 1895[2]. The exports returned after that date, i. e. after the occupation of Formosa by the Japanese, doubtless include some camphor grown in Formosa, so that they cannot be regarded as reliable figures for Japan proper. For this reason, we would only mention the following particulars: — In 1907—8, 1618 families were engaged in camphor production in Japan, and the production of crude camphor was 987922 lbs. In 1910—11, 2615 families produced 1394896 lbs., in 1915—16, 4239 families produced 2117878 lbs.; in the following year, 4329 families only produced 2074113 lbs., and in 1917—18 only 3274 families were engaged in the industry, and the production fell to less than 1300000 lbs. — For 1919—20a yield of 4000000 kin (5291000 lbs.) was anticipated, and a return to the normal yield of 5000000 to 6000000 kin (6615000 to 7938000 lbs.) for the next year. It is not to be expected that any considerable share thereof will enter foreign commerce. In 1918, the Japanese industry consumed 9600000 lbs. of crude camphor, and in May 1920 all export of crude camphor was prohibited, a limited amount of refined camphor being allowed to foreign refiners at a discount of 3 per cent. below the market price. In former years nearly all the camphor was exported, whereas in China the export was only one-fourth of the quantity produced.

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[1] *Drug and Chemical Markets* 9 (1921), 1206. — [2] Comp. also statistics in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, page 473.

As stated already in previous *Reports,* the Japanese Monopoly Board had started since 1900 planting camphor trees on a large scale, hoping for a great success[1]). But in 1918 it is admitted that the expectations to be able to obtain camphor from the leaves had not been fulfilled and that the camphor obtained from young trunks was not satisfactory. The yield to be obtained from the planted camphor trees, even in another 10 to 15 years, will most likely not be so considerable either, as generally pretended. The trees will by then be about 35 years old, whereas the highest yield is not arrived at till they are 60 years old.

Formosa exported 6 927 000 lbs. of camphor in 1895, compared with 7 860 000 lbs. in 1913, and the following table shows the exports for the years 1915—1919.

Production and Export of Formosan Camphor

		to the United States	to Europe	to Japan
1915/16 . . .	10 389 521 lbs.	4 211 766 lbs.	1 798 277 lbs.	4 379 478 lbs.
1916/17 . . .	11 506 447 „	6 525 489 „	1 726 997 „	3 253 961 „
1917/18 . . .	7 945 890 „	4 129 027 „	1 045 345 „	2 771 518 „
1918/19 . . .	6 137 732 „	2 055 188 „	913 021 „	3 169 523 „

According to *Commerce Reports*[2]), it is supposed that the camphor production in Formosa amounted to 6 million lbs., from April 1st 1920 to March 31st 1921, exceeding that of the previous year by 275 000 lbs. The export, which in July 1920 amounted to 480 000 lbs., rose till March 1911 to 600 000 lbs. monthly. In the expectation that the celluloid industry will revive as soon as the present stocks will have been cleared, the Monopoly Board means to increase gradually the quantity of camphor produced. Already towards the end of the Chinese administration in Formosa, there existed a monopoly for camphor, but as it sustained considerable losses, owing to its reckless exploitation and inadequate methods of production, an own monopoly system was created for the island in 1899. In 1903 a joint Monopoly Act was passed for Japan and Formosa.

The number of camphor trees growing in the public and imperial forests of Formosa is estimated at 12 millions, said to correspond to $2^1/_2$ (??) million cubic feet of wood. The other camphor trees in Formosa, from 100 years of age upwards, are supposed to represent 30 million cubic feet of wood, out of which 17 500 tons of camphor and 12 800 tons of camphor oil might be obtained[2]).

The Government spends 50 000 yen annually for planting young camphor trees in Formosa. More than 30 000 acres have been planted, whereas in Japan proper there are only 2000 acres with such plantations. The Government approved of a plan to plant 5000 *tsubo* (1 tsubo = 2.5 acres) with camphor trees annually for 11 years from 1918, to protect all the wild trees and to reduce the export as much as possible.

The production of camphor in Formosa is dealt with in two articles by H. J. Shepstone[3]) and A. B. Kirjassoff *("Formosa the beautiful")*[4]). The illustrations regarding the whole process of camphor production, as given in Kirjassoff's treatise, are specially interesting and instructive. As Shepstone reports, there are nine tribes in Formosa, all of which are hostile to each other, and the largest and most powerful is the Atayals, who number about 30 000, occupying an area of 2500 square miles in the northern part of the island, much of which has never been explored. Head-hunting is the most glorious thing in their lives, and a lad is not an adult until he secures a human head. The seriousness

[1]) Comp. *Reports* 1918, 12; 1919, 11. — [2]) *Deutsche Allgem. Ztg.* According to *Chem. Industrie* 44 (1921), 413. — [3]) *The World's Work,* Oct. 1921. As per *The Chemist and Druggist* 95 (1921), 568. — [4]) *The National Geographic Magazine* 87 (1920), 241.

of their attacks on the camphor-gatherers may be gauged from the fact that during 1914, when the statistics were last available, 187 of the collectors were killed and 190 wounded.

In order to reach the large tracts of camphor forests in the interior, it was essential to overcome the savages. The method employed was the establishment of a "guard line" all round the mountainous interior, with small military outposts at intervals, and this artificial frontier has gradually been extended, so that the turbulent natives are confined in a slowly-diminishing area. As this method was too slow, in view of the present state of the industry, the Japanese Government recently voted £ 1000000 to bring about a more rapid pacification of the savages, and troops have been sent in large numbers. The Formosan native must, therefore, quickly change his attitude towards the camphor-gatherers or suffer annihilation. The Government is anxious to improve the lot and condition of the natives and to provide education for their children.

Shepstone says that an average camphor-tree, with a basal circumference of 12 feet, will yield about 3 tons of camphor. The felled trees are chopped into chips and subjected to distillation on the spot. The chips are placed in a retort over boiling water, and, as the camphor vaporizes, it passes through pipes into submerged vats, which are so arranged that cool water from a mountain stream can run over them to accelerate crystallization[1]). After the camphor has crystallized, the vats are opened, and the product is placed on wooden troughs, to allow whatever free oil there may be to drain off. This oil will yield 90 per cent. of crude camphor in the process of refining. The crude camphor is packed in tins and carried down precipitous mountain paths on coolies' backs to the nearest railway line, whence it goes to the Government refinery at Taihoku.

There are 80000 stills scattered over Formosa. They are in the hands of Chinamen, whereas the tree-fellers are Japanese.

As the Philippine Islands apparently offer favourable conditions for the cultivation of camphor-trees, the Government has granted a large stretch of land for this purpose to an American company.

In Ceylon, Nock had begun in 1893 to cultivate camphor-trees in the Hakgalla Gardens, six miles from Nuwara Elya, at a height of 5600 feet. The tree thrives best at a height of 3 to 5000 feet on chalky soil, also containing potash. As it is not sensitive with regard to wind, it is often found as a sort of wind-screen for tea plantations[2]). The twigs and branches yielded 2.7 to 3.4 per cent. of camphor oil and 0.75 to 1 per cent. of camphor. The output amounted to 143 to 190 lbs. of camphor. Bamber and Willis stated in 1910 that the cultivation of camphor-trees was successful in Ceylon, if they were plated in rows facing the direction of the predominating winds, on sandy clay often watered by rain. Within five years they attain a height of 18 to 20 feet.

It seems that at least three different kinds of camphor-trees are cultivated in the West-Indies. A tree in St. Vincent, supposed never to have bloomed, over 100 years old, and which had been determined in Kew as *Cinnamomum Camphora*, var. *glaucescens*, yielded on distillation of the wood only oil, but no solid camphor. Another, also inferior kind in Trinidad and Dominica is conspicuous by its reddish shoots and leaf-stalks and its oval leaves which, on being crushed, smell of turpentine oil. However, there are also trees on these two islands, as well as in Jamaica, the leaves of which yield 1 per cent. of camphor or more.

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[1]) It is to be seen from this description that it refers to an improved kind of the usual Chinese distilling apparatus, originally employed in Formosa. In Japan proper the production of camphor has been further improved. (Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, page 456.) — [2]) Comp. *Report* 1918, 15.

Cinnamomum Camphora is cultivated all over Queensland, where another new species occurs, *Cinnamomum Oliveri*, which is said also to contain camphor.

In New South Wales, the fresh leaves of a tree, 15 years old, yielded 1.02 per cent. of camphor.

A remarkable camphor-tree is found on an island in the Lago Maggiore. When eight years old, its trunk was 1 foot in diameter and had the extraordinary height of 90 feet. Camphor-trees also grow in Buenos Aires, the Canaries and Madagascar. On the latter island the wood of trees over 50 years old is used as building material.

The first camphor-tree plantation in Satsuma, Florida, put 10000 lbs. of camphor on the market since the beginning of this year. The product is stated to be equal in every respect to the Japanese refined camphor. Two companies are said to have 2500 acres each under cultivation. A third company has been granted permission to start a large plantation in Texas[1]).

According to the *Revue agricole de l'Afrique du Nord*[2]) several hectares in the Doumia Woods (Algeria) have been planted with camphor-trees in 1919. The success obtained there, as well as in the districts of Algiers, Blida, Boudjia, El Miliah and El Hanser, are supposed to induce the Government to substitute more and more the camphor tree to the cork-oak in the coastal regions of Algeria, especially in the moist East, where the cork of the oaks is always damp and therefore of no value. According to Trabut it would be possible to obtain from a camphor-tree plantation, when 25 years old, 300 kilos each of camphor and camphor oil per hectare[3]).

According to S. T. Dunn[4]), it is stated that the direct cause of the presence in the camphor-tree of essential oil of varying constitution and quantity is to be found probably in the formation within the plant of terpentinol ($C_{10}H_{16}$)[5]), which is gradually changed by the activity of the living cells into camphor ($C_{10}H_{16}O$). As this oxidation progresses, different compounds appear, and it is by their admixture in the products of distillation that all the different oils and finally camphor itself is formed. "If this theory is accepted", Mr. Dunn observes, "it is not surprising to find that the yield of camphor varies from month to month." Cases are cited to prove that in certain countries, notably Japan and Formosa, much more camphor is obtained from camphor-wood cut in the cool season than from that cut in the summer. Any other circumstance affecting the healthiness and cell activity of *Cinnamomum Camphora* will, it is pointed out, on the above theory, also affect the yield of camphor. It is suggested, for example, that fungal disease of the wood may have a deterent effect on the production of camphor, and it is also noticed, in this connection, that the climatic conditions of North Formosa seem to favour a plentiful production of solid camphor, whereas in the South, many trees yield little solid camphor, but large quantities of Sho oil and Yu-yu oil, the trees being known to the Japanese as Sho-gyu and Yu-yu, respectively[6]). In the climate of Florida the same species produces solid camphor mixed with an oil differing from the Japanese oils in its low percentage of safrole. Remarkable variations of camphor content in the leaves of trees growing under different conditions of shade and soil have also been recorded[7]). Experiments in Kew have shown that, apart from two slight colour

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[1]) *Journ. Soc. Chem. Ind.* 40 (1921), R. 388. — [2]) *Parfum. moderne* 14 (1921), 212. — [3]) Comp. *Report* April 1908, 23; *Bericht* (German ed.) 1920, 13. — [4]) *Bull. of Miscellaneous Information* no. 4, 1921. As per *Perfum. Record* 12 (1921), 323. — [5]) The designation of "terpentinol" for hydrocarbons $C_{10}H_{16}$ is, of course, absolutely incorrect. — [6]) According to K. Nagai, the Shô-Gyu and the Yu-Ju trees, the botanical origin of which is still unknown, are not identical with *Cinnamomum Camphora*. The Yu-Ju oil has a great resemblance with camphor oil. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, page 672. — [7]) Comp. also *Report* 1918, 15.

indications, no visible varietal characters can be found in any part of the tree to separate "camphor" trees from "oil" trees. Dunn suggests the following lines of improvement for plantations of camphor trees: (1) Seeds should be secured from trees known to produce camphor, (2) suitable climate and soil should be selected, (3) saplings must be planted so that they may be clipped conveniently; (4) the best months for clipping must be ascertained by experiment, as observations show considerable changes in the camphor content of the leaves as the growing season advances.

Cananga Oil. — It is reported that the distillation of this article in Java is no longer remunerative at the present price obtained for it in Europe, *i. e.* 10 to 12 Dutch Florins per kilo, especially because the producers lack cheap fuel. According to our informants, the distillation stopped almost completely in 1921, all the oil shipped being of 1920 production. As the wages for the collectors of the flowers have doubled since the war, the distillers prefer waiting until they know the consumers' attitude with regard to the higher prices that are to be expected.

Caraway Oil. — The Dutch caraway market was very firm throughout the year 1921. Owing to the small crop (only 15000 bales, *i. e.* even less than in the previous year), the prices rose during the summer up to about 17 florins, but towards the end of the year they went down a little, to 16 florins, as there was no very keen demand. The stocks of old caraway, which had agglomerated considerably, as we reported previously, have gradually been disposed of, so that the average quality was better than in 1920. One expects very little of the 1922 crop, in fact less than the year before, as the seedlings from spring 1921 had to be ploughed under, owing to the drought in autumn. The quantities available up to the next crop but one, *i. e.* in August 1923, will most likely prove insufficient for the world's requirements, so that very high prices are to be expected.

As regards the caraway market in 1920, some information from the Dutch Board of Agriculture is now available[1]), from which we gather that the area under cultivation was 971 hectares. The crop was small, but there were still considerable stocks of old seed. There was but little business with Central Europe; England and the United States, however, took again the usual quantities. The prices ranged from 22 down to 15 florins. Owing to high rent, big wages and expensive manure, the cultivation is said to have become unprofitable, so that it is to be feared that it will be given up. The exports in 1920 totalled 3767 tons to the value of 1412000 florins.

There were fairly considerable offers of East-Friesian and East-Prussian caraway, but unfortunately the largest part by far was exported, as the prices paid abroad were tempting. Only comparatively small lots were available for distillation in the country. It is to be regretted that the German Government have not realized so far, how necessary it is to stop the exports of caraway seed. On the other hand, one is pleased to see that the German farmers have given far more attention to the cultivation of caraway and that the success is visible already.

Oil of Cathetus fasciculata. — In the course of this year we received two samples of the so-called *Bruyère* oil, distilled in Annam (Further India) from the *Euphorbiacea Cathetus fasciculata*, Lour. As the oil is but little known, we think the following particulars will be of interest: — The samples were pale yellow and yellow, respectively,

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[1]) *Verslag omtrent Handel, Nijverheid en Scheepvaart van Nederland gedurende* **1920.**

and their odour recalled cajuput oil, $d_{15°}$ 0.8826 and 0.8905, α_D —2°9' and —5°26', $n_{D20°}$ 1.47730 and 1.47926, acid v. 1.1 and 1.8, ester v. 4.3 and 4.2, soluble in 0.5 and 3.5 vols., respectively, of 90 per cent. alcohol. Of 80 per cent. alcohol even 10 vols. were insufficient for a solution.

These properties tally on the whole with the indications regarding *Bruyère* oil in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, page 146.

Chamomile Oil. — According to an English periodical[1]), oil of chamomile is a suitable solvent for platinum chloride. It is said to be used for this purpose in the glass and porcelain industries, in order to coat vessels with platinum.

Chenopodium Oil. — See Wormseed Oil, p. 80 of this *Report*.

Cinnamon Oil, Ceylon. — The demand for cinnamon oil and, in a still higher degree, for cinnamon leaf oil has increased considerably during the last years. The latter can be obtained in a satisfactory quality from Ceylon, the Seychelles and Mauritius, whereas it seems to be impossible so far to distil a good bark oil from raw material of other origin than Ceylon, although it is reported that cinnamon bark from the Gold Coast has yielded in the last years valuable oils of agreeable odour[2]). The area planted with cinnamon trees in Ceylon has decreased continuously, as other plants, like caoutchouc-trees and coconut palms pay better. The latest official estimate[3]) of the total area under cinnamon is about 35000 acres, as compared with 48000 acres in 1909. The cinnamon gardens of Ceylon are situated chiefly in the Southern and Western Provinces of the island. The following tables give details of the exports from Ceylon:—

Annual average export of cinnamon bark from Ceylon during the decades

1841 to 1850	529 461 lbs.	52 497 £[4])
1871 „ 1880	1 274 668 „	64 649 „
1881 „ 1888	2 088 232 „	107 604 „
1901 „ 1910	5 565 684 „	171 395 „
1911 „ 1920	5 155 470 „	134 760 „

Exports from Ceylon

Year	Cinnamon bark[5])		Cinnamon bark oil[6])		Cinnamon leaf oil	
1909	6 501 040 lbs.	181 913 £	—	—	—	—
1910	6 306 060 „	186 219 „	90 710 oz.	1618 £	76 008 oz.	519 £[4])
1911	5 773 140 „	139 086 „	49 502 „	1131 „	63 600 „	453 „
1912	5 945 632 „	188 992 „	65 972 „	1417 „	34 020 „	186 „
1913	5 140 800 „	160 908 „	16 112 „	715 „	52 092 „	354 „
1914	4 080 272 „	107 777 „	10 129 „	673 „	36 936 „	228 „
1915	6 451 984 „	133 178 „	36 343 „	1698 „	64 692 „	1061 „
1916	5 012 896 „	83 713 „	62 132 „	1620 „	120 874 „	1809 „
1917	3 328 192 „	64 518 „	78 438 „	2655 „	95 091 „	1199 „
1918	4 187 680 „	89 900 „	62 283 „	5109 „	258 020 „	5048 „
1919	7 700 560 „	246 393 „	66 773 „	5655 „	299 928 „	6274 „
1920	3 933 552 „	143 141 „	73 246 „	2572 „	365 976 „	5553 „

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[1]) *Perfumer's Journ. & Essential Oil Recorder*. As per *Deutsche Parf. Ztg.* 7 (1921), 95. — [2]) Cf. *Bericht* (German) 1920, 66. — [3]) *Bull. Imp. Inst.* 19 (1921), 319. — [4]) Converted from rupees at the rate of Rs. 15 = £ 1. — [5]) Cinnamon bark includes quills and chips. — [6]) The cinnamon bark oil exported from Ceylon was as a rule strongly adulterated with cinnamon leaf oil.

Before the war Germany was, as a rule, the largest buyer of both quills and chips; other important countries to which the bark was shipped being the United Kingdom, Spain, Holland, Italy, the United States and Belgium. In 1920 Germany again became an important buyer 218736 lbs. of quills and 134176 lbs. of chips, against 4928 lbs. of quills in the year before, in that year the United States being the chief buyer of quills.

The best cinnamon is grown in Ceylon in a very sandy clay or fine white quartz sand, with a good rich sub-soil, at altitudes of less than 1500 feet, in the strip of land 12 to 15 miles wide, on the south-west coast, between Negumbo, Colombo and Matura. The tree is usually grown from seed in nursery lines and transplanted when 3, 4 or 12 months old. Sometimes it is propagated by cuttings of very young three-leaved shoots, or by layers. Adult trees flower in May and fruit in July; and, unless bagged for seed, the entire crop of fruit is liable to be eaten by birds. The ripe fruit is heaped in the shade until the pulp turns black and rots, when the seed can be removed by trampling; the seed is washed and dried in the shade before sowing. — Cattle, goats and squirrels nibble the young shoots; but otherwise cinnamon is not very liable to animal or vegetable pests. *Pestalozzia cinnamomi*, Raciborski, is a minute leaf and twig fungus; and the "pink disease" (*Corticium salmoni-color*, B. and Br.), a wet season disease, well known as attacking Para rubber, forming a pink crust on the stem and destroying the cambium, a sign that the trees are over-crowded, also occurs and can be dealt with by spraying with Bordeaux mixture and excising and burning affected parts.

In order to obtain the bark, the shoots, usually two years old, averaging 3 to 4 feet in length and 0.5 to 0.75 inch in diameter, are cut in May or November, when the sap moves and facilitates peeling. The slips of bark are heaped together and covered over for a day or two, so as to undergo, perhaps, a slight fermentation[1] which facilitates the scraping off of the epidermis and pulpy hypoderm in the process known as "piping". The slips of bark contract into pipes or "quills", which are packed one inside the other, cut square and of uniform length, dried in the shade and ultimately in the sun, and eventually made up into bundles of 100 lbs. weight. The prunings and waste pieces obtained in peeling are known as cinnamon chips. They have only been exported from Ceylon since 1867 and have been used since 1872 chiefly for distilling cinnamon oil[2].

There is no evidence of the cultivation on any commercial scale of the true cinnamon *(Cinnamomum zeylanicum)* in India, though it may be represented as a wild tree in the Western Ghats. But various barks and twigs are sold as *Cassia lignea* originating from other Cinnamomum species, such as *C. Tamala*, Nees et Eberm., *C. obtusifolium*, Nees (closely allied to *C. Cassia*, Blume), *C. iners*, Wight[3] (according to Thwaites and Ridley only a coarser form of *C. zeylanicum*, like *C. nitidum*, Blume, and some others)[4] and *C. macrocarpum*, Hook. fil. The essential oils of these drugs are used partly for adulterating the genuine cinnamon oil, partly in the soap industry.

Cinnamon trees were introduced into Seychelles with other species, about 1775, from the Dutch East Indies, and were for a time cultivated in the Royal Gardens at Mahé. The trees spread through the forests and were neglected until 1908, in which year 1202 tons of bark were exported. At the same time distillation of oil from the bark of the wild trees was commenced. The bark differed but little in appearance

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[1] The fresh white bark turns red on drying, owing to the formation of phlobaphene. A fermentation is not very likely to occur. — [2] Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 419. — [3] According to the *Index Kewensis, Cinnamomum iners*, Wight, is identical with *C. zeylanicum*. — [4] Dymock, *Pharmacographia Indica*, 1893, vol. III, p. 208.

from that of the trees cultivated in Ceylon[1]), but it was never handled so carefully, never had the fine aroma of Ceylon cinnamon[2]) and in consequence never fetched so good a price. The exports of bark from Seychelles for the years 1908—1919 are shown in the following table: —

1908 . . . . 1202 tons	1915 . . . . 189 tons
1909 . . . . 1044 „	1916 . . . . 184 „
1910 . . . . 731 „	1917 . . . . 1 „
1911 . . . . 964 „	1918 . . . . nil „
1912 . . . . 1098 „	1919 . . . . 275 „
1913 . . . . 698 „	1920 . . . . 185 „
1914 . . . . 589 „	

Prior to 1915 most of the bark was shipped to Germany, Holland being the next most important customer. In 1915 and later years the bulk went to the United Kingdom. After twelve stills had been installed in 1915 for the distillation of cinnamon bark and leaf and lemongrass oils, the exports increased sevenfold within three years. During the war the development of the industry was hampered by the impossibilty of obtaining modern machinery for steam distillation from Europe, but a Chinese settler set the example of building a small still of wood and iron obtained locally for direct fire distillation: his example was followed by many small-holders. On samples being submitted to the Imperial Institute, it was found that there was not much difference between the oils obtained by steam distillation and those from direct fire distillation. The high price reached by cinnamon leaf oil encouraged the manufacturers to devote themselves mainly to this oil, as is shown by the following table of exports, and during 1920 there were 44 distilleries at work (total production 24 430 litres)[3]), as against 12 in 1915.

Export of Cinnamon Oils from Seychelles.

	Bark oil			Leaf oil		
1911	1 l	0,2 £ .		212 l	56 £
1912	—	— .		1 543 „	338 „
1913	— .	—		3 054 „	799 „
1914	—	—		8 406 „	2 320 „
1915	99	73	„	9 587 „	2 505 „
1916	1834 „	1041	„	15 669 „	4 484 „
1917	91 „	171	„	14 175 „	4 317 „
1918	131 „	262	„	12 731 „	5 111 „
1919	27 „	46	„	24 430 „	11 634 „
1920	—	—		39 507 „	26 029 „

The price of cinnamon leaf oil having fallen from 10 rupees to about Rs. 3 to Rs. 4 per litre in 1920[4]), little has been manufactured since, so that the exports for 1921 will show a decline.

Up to 1911 no difference was made in Seychelles between bark and leaf oils. The exports of "cinnamon oil" were 285 litres in 1908, 12 litres in 1909 and 124 litres in 1910.

A number of trees having been planted near Malacca, a small quantity of quills were prepared in 1851 by Sinhalese convicts, who were professional cinnamon peelers, and sent to England, but although, considering that the bark was cut at the wrong season and from neglected trees, the report was favourable and the bark was paid

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[1]) Cf. *Reports* April 1910, 35; April 1911, 43. — [2]) Cinnamon oil from Seychelles differs also from the Ceylon product in that its content of cinnamaldehyde is lower and that it contains camphor. *Report* November 1908, 42. — [3]) As per *Heil- und Gewürzpfl.* 4 (1921), 127. — [4]) *Perfum. Record* 12 (1921), 415.

fairly well, the cultivation was not proceeded with, probably on account of the low prices which have since prevailed. — Various other species of *Cinnamomum* occur in a wild state in the Malay region, some of which, such as *C. tavoyanum*, are akin to *C. Cassia*, whilst others, such as *C. Parthenoxylon*, are more allied to *C. Camphora*. *C. Culilawan*, Blume, the clove bark[1]) of the Malays (*Kulit* = bark, *Lawang* = clove) is a native of both the Peninsula and the islands. The calyces of the fruit are used locally in medicine and curries under the name of *"bunga lawang"* (clove flowers).

The cultivation of *Cinnamomum zeylanicum* was introduced into the Dutch East Indies (Java) in 1825, as it seemed with success in the beginning. It resulted afterwards, however, that the fine quality of the genuine Ceylon cinnamon could not be attained, and from 1865 the cultivation gradually died out. The tree is now grown only on a small scale on a few European estates. — A trifling quantity of bark is derived in Java from *C. Cassia* and the rest from *C. Burmanni*, Blume[2]), a tree growing wild throughout the Malay archipelago. It is a slender tree occurring chiefly in the mountains, and the bark is stated to improve in quality the greater the altitude at which it is grown. The better qualities of bark are from the trunk, the second quality, which is lacking in flavour, being derived from the thicker branches. The United States has been the chief purchaser of the product, Holland taking the bulk of the remainder.

Total Exports of Cinnamon Barks from the Dutch East Indies (Padang, Java and Macassar) in the years from 1908 to 1912: —

1908	. . .	752 tons	= 22916 £
1909	. . .	1016 „	= 32833 „
1910	. . .	1297 „	= 37333 „
1911	. . .	1922 „	= 22250 „
1912	. . .	1032 „	= 23666 „

Both *Cinnamomum zeylanicum C. Cassia* have been successfully grown in Fiji from seed, and the bark and the leaves distilled on a small experimental scale at Nasimu[3]). The cinnamon was planted in 1906, and is stated to have become quite naturalized, the seeds being distributed through the forests by pigeons.

As to the West Indies, cinnamon was found by Captain Marshall in 1782 in St. Domingo. It was sent to Jamaica and has since been grown in the island, but not on any considerable scale. A bark frequently known in the drug trade as "wild or white cinnamon", is that of *Canella alba*, Murr., a *Winteranacea*, in no way related to the true cinnamon. It is a native of Florida and the West Indies, and has been known as "Jamaica Winter's Bark" and "Jamaica Cassia lignea" but is now shipped mainly from New Providence in the Bahamas under the names of "White Wood Bark" or "Cinnamon Bark".

Some data from an English source[4]) as to the history of cinnamon barks[5]) which, as it is well known, belong to the oldest spices, will certainly interest our readers. According to D. Hanbury none of the cinnamon of antiquity was derived either from *Cinnamomum zeylanicum* or from Ceylon. The very name "cinnamon" from the Arabic *"mama"* or Greek *"amomum"* (meaning spice) and the prefix *"chini"*, Chinese, which persists in the Persian and Hindustani *"Darchini"*, suggests the Chinese origin of the drug, and under the name *"Kwei"*, which forms part of several Chinese place-names,

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[1]) The essential oil of this bark contains 62 per cent. of eugenol and some methyl-eugenol. Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 439. — [2]) As to oils from the bark of *Cinnamomum Kiamis*, Nees = *C. Burmanni*, Blume, see Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 438. — [3]) *Rept. on Agric., Fiji*, 1911, p. 7; 1918, p. 6. As per *Bull. Imp. Inst.* 19 (1921), 338. There are no further particulars in this publication. — [4]) *Bull. Imp. Inst.* 19 (1921), 321. — [5]) Cf. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 125.

cassia is mentioned in the earliest Chinese herbal, said to have been written in 2700 B.C. The mention of *"Tien-chu kwei"*, that is Indian cassia, in the *Pen-tsao*, written in the eighth century may refer to bark produced in Malabar. The mention of two spices or perfumes, cinnamon and cassia, in the older books of the Old Testament and in the earliest Greek works on medicine, as nearly allied but of different value, may have only referred to two qualities of what we should now call cassia, this latter name — originally *"casia"* — being related to the Hebrew *"ketzioth"*, meaning "stripped off". The barks were originally brought to Europe — that is to the Levant — by Phœnicians, who obtained them from the Arabs, and the ancient notion that they were derived from a *"regio cinnamomifera"* in Somaliland may have been merely an error arising from this trade passing through several hands or part of the common characteristic system of trade mystification. The full Arabic name *"Kirfat-et-darsini"*, bark of the Chinese tree, shortened into *"Kirfah"*, persists as *"Kalfah"*, the existing Bombay name for Malabar cassia. As Sir Emerson Tennent pointed out, there is no mention of cinnamon as a product of Ceylon prior to the Arab writer Kazwini, about A. D. 1275, and the Minorite friar, John of Montecorvino, about 1293; and Hanbury makes the highly probable suggestion that the Chinese, who were acquainted with *C. Cassia*, a very similar tree, and who traded with Ceylon and the coast of Malabar, were concerned in the discovery of the value of the Ceylon bark. The Chalias, the caste to which the peeling and preparation of cinnamon bark is now restricted in Ceylon, are said to have emigrated from India in the thirteenth century; and in the following century Mohammedan writers were well acquainted with Ceylon cinnamon and the difference between it and Chinese and Indian cassia. One of them, writing in 1368 of *"Darchini"*, says "the best is that which comes from Ceylon", while the best Chinese cassia *("salikheh")* is, he says, thick, reddish, a little bitter and astringent, but sweeter than Indian Kirfah which "tastes like cloves".

The Portuguese, arriving in Ceylon in 1505[1]), found the cinnamon in a wild state, and exacted a tribute of 250000 lbs. of bark annually from the Sinhalese king. Garcia da Orta, about the middle of the same century, speaks of Ceylon cinnamon as worth four times as much as that from Malabar, and the Portuguese occupation of Ceylon in 1536 is stated to have been accomplished chiefly for the sake of the cinnamon. After the Dutch conquest in 1656 the Government monopoly of the export of bark was strictly maintained, but it was under the Dutch auspices that, about 1770, the cultivation of the tree was commenced. The entire European demand, stated to have been about 400000 lbs. a year, was then supplied from Ceylon; and, after the British conquest in 1796, the annual production, during the monopoly of the East India Company, which lasted until 1833, did not exceed 500000 lbs. The Dutch began the cultivation of the tree in Java in 1825, and, while a heavy export duty was imposed on Ceylon bark until 1853, the competition of Javanese bark and of Chinese cassia told upon the Ceylon industry.

Cinnamon barks and chips from Madagascar, received by Roure-Bertrand Fils[2]), yielded on steam distillation 0.17 per cent. of essential oil of the following properties: $d_{17°}$ 0.9715, $d_{15°}$ 0.9731, $a_{17°}$ — 5°49′, acid v. 2.49, aldehyde content 48 per cent.; incompletely soluble in 70 per cent. alcohol, soluble in 1 vol. of 80 per cent. alcohol; on addition of more alcohol, turbidity which disappeared again, however, when the quantity of alcohol reached 10 volumes.

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[1]) Vasco da Gama reached the coast of Malabar already in 1498. — [2]) *Bull. Roure-Bertrand Fils,* October 1921, 35.

From the distillation water 0.3 per cent. of an entirely different oil could be extracted with light petroleum: d_{17^0} 1.0281, d_{15^0} 1.0297, $\alpha_{16^0} - 2^0\,2'$, acid v. 2.49, aldehyde content 82 per cent., soluble in 1.75 vol. of 70 per cent. alcohol and in 0.75 vol. of 80 per cent. alcohol, further addition of alcohol caused slight turbidity. A mixture of both oils had the following constants: d_{17^0} 1.0075, d_{15^0} 1.0091, $\alpha_{17^0} - 3^0\,23'$, acid v. 2.49, aldehyde content 70 per cent., soluble in 2 vols. of 70 per cent. alcohol; slight turbidity on further addition of alcohol. The oils referred to were amber-yellow, their odour reminded one somewhat of Ceylon cinnamon oil, but they did come near the quality of the latter.

Cinnamon Leaf Oil. — Little has been published so far on cinnamon leaf oil from South Kanara; the more interesting therefore what C. K. Menon[1]) says about it. The cinnamon tree, *Cinnamomum zeylanicum*, Nees which according to Tschirch occurs in the south-west of British India in very different forms[2]), all belonging to the same species, however, grows abundantly in the coast district of South Kanara at elevations varying from 100 to 700 fest — and fairly up to 3500 feet on the Ghat slopes. The local distillers distinguish four kinds of trees from the taste of the leaves, *viz., "mitta"* (sweet), *"pickka"* (insipid), *"tej"* (pungent), and *"kadira"* (bitter). They collect the leaves only of the last two for oil extraction, the first two are reported to be useless for this purpose. In Ceylon the leaves are macerated in sea-water and subsequently distilled, but in South Kanara the first operation is not carried out. In that district the rude apparatus for distilling the leaf oil consists of three earthen pots, serving respectively as boiler, covering pot and receiver, with two short bamboo tubes to conduct the steam from the boiler to the condenser. The large earthenware pot which acts as the boiler is placed over a furnace; water is poured into it to a depth of 9 inches. Fairly matured green leaves are packed into it. A small earthenware pot is kept with its mouth down over the boiler, the joint being well plastered with clay and cow-dung mixed. A small bamboo tube, about a foot long and half an inch in diameter, is thrust through a hole in the top of the upper pot. To the free end of this tube, another about three feet in length is attached, the two joints being wrapped up in cloth and plastered well with the clay mixture. The longer tube is led into the condenser, fixed in a tank containing cold, muddy water. A thick wet cloth is spread over the mouth of the condenser, and around the bamboo tube. The muddy water is replaced as it gets heated. The water in the boiler is heated to boiling point; the steam and the extracted oil are condensed against the cool sides of the condenser. The oil being heavier than water, sinks to the bottom.

The working season lasts only from November to March, after which the young leaves appear, and these would not yield sufficient oil to repay the labour. In North Mangalore Forest Division of the South Kanara district cinnamon areas in the unreserved lands are divided into working circles; each one is intended to provide leaves for five stille annually during the working season. The number of local distillers is fixed, and each working circle is auctioned to a single individual.

Menon suggests that cinnamon growth should be concentrated within small and compact areas, instead of continuing the present system. The plant can easily be grown from seed. The average annual production is about 25 tins of oil (1 tin = 24 bottles = 18 litres), which is sent to Bombay, the chief market for South Kanara oil.

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[1]) *Perfum. Record* 12 (1921), 31. — [2]) Cf. also page 20 of this *Report.*

Citronella Oil from Java. — The Java export figures from January up to the end of November 1921 have now been published as follows: —

Holland.	30373	kilos
Great Britain.	8356	„
Germany	10040	„
France	26331	„
United States	92118	„
Singapore	8391	„
China	8235	„
Japan	64029	„
Other countries	889	„
	248762	kilos.

The exports in the last three years totalled: —

1918	=	228000	kilos
1919	=	528500	„
1920	=	434500	„

the separate figures being: —

Destination	1918	1919	1920
Holland	—	233000	124000
Great Britain	—	91000	75000
France	—	69000	80000
Switzerland	—	6000	—
United States	84000	85000	76000
Singapore	46000	24000	44000
Hong Kong	5000	6000	1000
China	4000	2000	9000
Japan	81000	7000	19000
Australia	1500	3000	4500
Germany	—	—	—
Other countries	6000	1000	—

The low figures for Germany are explained by the fact that she had no direct steamer connection with the Dutch Indies during the period referred to. Her real consumption is contained in the figures given for Holland.

Australia bought as long as there was little or no Ceylon oil available. Singapore and Hong Kong are only places of transit.

As it will be remembered, the total export of Java citronella oil was 426000 kilos in 1916 and 515000 kilos in 1917. The diminution by nearly 300000 kilos in 1918 was due to shipping difficulties, which were overcome only gradually in the course of 1919. Since then the costs of production have risen considerably, owing to the upward movement of the wages in 1919 and 1920. Besides, various factories of medium size have become State property by repurchase or expropriation on account of older claims and they have been closed, as such factories do not lend themselves to be managed by the State. A somewhat correct estimate of the total production can only be based on the average export figures of several years, the available data regarding the area under cultivation being inaccurate. In competent quarters the average annual production is estimated at 350000 kilos, for the distillation of which 60000 tons of citronella grass would be required, supposing a yield of 0.6 per cent. The total production in 1921 is stated to have been about 320000 kilos.

Of the above-mentioned shipments of 248762 kilos for the time from January to November 1921, only 82000 kilos were forwarded during the first six months, as the prices then left very little profit. Business revived as soon as the market improved.

The production is said to have gone down considerably during the summer months, owing the extraordinarily dry weather.

A citronella oil from the Seychelles of the year 1918, investigated by the Imperial Institute[1]) had the following constants: — d_{150}^{150} 0.881, α_{D200} — 28° 30′, soluble in 1.7 vols. 80 per cent. alcohol at 20°, turbidity with 10 vols., insoluble in 80 per cent. alcohol at 15°. Total geraniol (all acetylizable constituents calculated as geraniol) 52.2 per cent., geraniol 27.5 per cent., citronellal 24.7 per cent.[2]). Compared with other citronella oils, the sample resembled somewhat the Ceylon product. The citronella grass, from which the sample in question had been distilled, had been imported from Ceylon to the Seychelles.

Clove Oil. — For the time being there are no special reports on the Zanzibar clove market. — Only 10 to 15 tons of the Madagascar cloves come from the main-land, the larger part being gathered on the island St. Marie, situated near the north-east coast. The exports, chiefly to France, were 143 tons in 1918 and 499 tons in 1919. Although the shipments in December 1920 amounted to 87 tons, the whole 1920/21 crop totalled only 20 tons. The prospects for 1921/22 are said to be good[3]).

Oil of Coleus amboinicus. — According to F. Weehuizen[4]), the leaves of *Coleus amboinicus*, Lour.[5]) (*C. carnosus*, Hassk.), a labiata indigenous in Java, contain an essential oil (0.055 and 0.021 per cent.), in which the presence of carvacrol could be proved.

Copaiba Balsam Oil. — In order to avoid the often disturbing influence of con-centrated sulphuric acid, J. B. Luther[6]) carried out Turner's reaction for the determination of gurjun balsam oil in copaiba balsam oil as follows: — After having added 1 drop of a 10 per cent. solution of sodium nitrite to a solution of 4 drops of the oil in 1 cc. of glacial acetic acid, this was mixed at once with 2 cc. of glacial acetic acid containing 5 per cent. by volume of concentrated sulphuric acid. The presence of gurjun balsam is revealed at once by a violet colour. Copaiba balsam turns red within a short time[7]).

Coriander Oil. — Thuringian coriander was on the market in fairly considerable quantities, but the prices asked for were so high that our industry bought with the greatest reserve. The depreciation of the Mark caused in this case too that nearly the whole production was exported at high prices to the detriment of the home industry, for in the end the manufacturers of essential oils had to buy at export prices in order to replenish their stocks. It seems, unfortunately, that the Government little grasps the situation for, as with caraway and fennel, no reply has been given to a motion to stop the export.

In order to ascertain something about the effect of bleaching on coriander, J. A. Baker[8]) treated the drug with sulphur dioxide. It was found through quantitative experiments that the action of a 1 per cent. solution of sulphur dioxide during one minute was quite sufficient to bleach coriander. This process answered better than a twenty-four hours' dry treatment of the seeds with double the quantity of sulphur dioxide. Whereas unbleached coriander yielded on steam distillation 0.185 per cent. of essential oil, the aqueous distillate of the bleached drug smelled of sulphur dioxide

[1]) *Bull. Imp. Inst.* 18 (1920), 338. — [2]) It is not said how the determination was carried out. — [3]) *United States Commercial Reports* 1921. As per *Journ. Soc. Chem. Ind.* 40 (1921) R. 235. — [4]) *Recueil Trav. Chim. Pays-Bas et Belgique* 37 (1918), 355. As per *Angew. Botanik* 3 (1921), 107. — [5]) According to the *Index Kewensis Coleus amboinisus* is identical with *C. aromaticus*, Benth. — [6]) *Journ. Assoc. Off. Agric. Chem.* 41 (1921), 422. As per *Journ. Soc. Chem. Soc.* 40 (1921), A. 488. — [7]) Comp. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, page 620. — [8]) *Journ. Americ. Pharm. Assoc.* 10 (1921), 453.

and contained no oil at all. Even upon cohobation of the aqueous distillates no oil was obtained. The distillate, however, then had a very pleasant odour.

The hitherto undecided question, whether bleached coriander is, found on the market, could therefore, it seems, be solved with the aid of distillation. As far as our own experience with drugs goes, we have only found bleached hops and orris root, which of course were unfit for distillation.

Oil of Costus Roots. — In 1916/17 the Kashmir State Forest Department realized Rs. $3^1/4$ lakhs revenue from the export of costus roots, 4.524 maunds of 82 lbs. being marketed[1]).

Cubeb Oil. — A sample of this oil was examined by C. T. Bennett[2]) and was found to lack the characteristic taste and odour usually associated with this oil. The physical characters answered the requirements of the British Pharmacopœia (d 0.922; α — 38°; n_{D25o} 1.4965; 75 per cent. distilled between 250 and 280°). On adding a few drops of nitric acid to a solution in glacial acetic acid, the oil gave a distinct violet coloration, as is the case with oils containing gurjun balsam oil. On fractionation, the lower-boiling fractions showed a higher optical rotation than usually observed, the higher-boiling portions, however, which gave the gurjun balsam reaction, had a lower and more normal rotation. Further investigation revealed that the oil had been distilled apparently from genuine, but small and immature fruits of *Piper Cubeba*, whilst the Ph. Brit. requires that only fully-grown fruits should be employed.

Curcuma Oil. — From this oil, d^{19o}_{40} 0.9692, d_{20o} + 0° 21′ (in a 25 mm. tube), S.V. Hintikka[3]) obtained, on boiling with sodium ethylate, and after repeated distillation a pale yellow oil turning rapidly dark (b. p. 110 to 115° [8 mm.]) which on treatment with hydrochloric acid and washing with water boiled at 115 to 116° (10 mm.); d^{19o}_{40} 0.9481; n_D 1.50543. From this product, two semicarbazones were obtained, m. p. 129° and 153 to 154°, which furnished the following ketones: — *a)* b. p. 116 to 118° (10 mm.), d^{19o}_{40} 0.9493, α_{20o} + 8° 30′ (25 mm. tube), n_D 1.50177; oxime, b. p. 160 to 161° (15 mm.); *b)* b. p. 122 to 124° (15 mm.), d^{19o}_{40} 0,9479, d_{20o} + 6° 40′ (25 mm. tube), n_D 1.49951. Since the letter ketone yielded, on treatment with semicarbazide, semicarbazones, m. p. 153 to 154° and principally with m. p. 125°, the two ketones were considered to be identical. The difference in the constants of the ketone are explained by its great tendency to oxidize. The combustion of both semicarbazones pointed to the formula $C_{10}H_{18}O$ of the ketone.

On oxidizing the crude ketone (not treated with hydrochloric acid) with potassium permanganate the author obtained a ketone (semicarbazone, m. p. 203 to 204°) which appeared to be identical with Rupe's[4]) *p*-tolylmethylketone, in addition to a substance which, on heating beyond 300°, was decomposed without previous melting (terephthalic acid?). When treated with a hypobromite, the ketone yielded a small quantity of a body melting at 33 to 34° (curcumic acid?).

Erigeron Oil. — The abundant occurrence of *Erigeron canadensis*, L., in the neighbourhood of Miltitz induced us to distil this well-known weed.

The whole plant, when just beginning to flower, yielded 0.264 per cent. of oil of the following constants: d_{15o} 0.8720, α_D + 53° 56′, n_{D20o} 1.49922, acid v. 0.3, ester v. about 63.5 (the change of colour when titrating was rather indistinct), ester v. after acetylation 70.3, soluble in 5.5 vols. and more of alcohol of 90 per cent.

1) *Perfum. Record* 12 (1921), 51. — 2) *Perfum. Record* 12 (1921), 90. — 3) *Zur Kenntnis des Curcumaöls* I. Helsingfors 1921. — 4) Comp. *Report* April 1911, 57.

The herb without roots, but flowering more abundantly, yielded about the same quantity of oil (0.26 per cent.). It was a little heavier and seemed to be strongly predisposed for resinification: $d_{15°}$ 0.8836, $\alpha_D + 50° 4'$, $n_{D20°}$ 1.50624, acid v. 0.3, ester v. about 70.9 (see above), ester v. after acet. about 81.9, soluble in 4 vols. and more of 90 per cent. alcohol with slight turbidity.

Both oils were brownish yellow and smelled feebly aromatic. When diluted their odour somewhat resembled that of neroly. No similarity with caraway, however, noticed with oils previously distilled[1]), could be stated.

Essential Oils, Sicilian and Calabrian.

The exports from the chief shipping place Messina in 1921 presented the following aspect: —

Destination	Lemon oil Kilos net	Bergamot oil Kilos net	Orange oil Kilos net	Mandarin oil Kilos net	Other Citrus oils Kilos net
Argentina	3197	776	97	—	60
Austria	188	116	50	—	—
Belgium	1119	396	293	—	—
Canada	3517	246	—	—	—
Denmark	2264	540	509	—	—
Egypt	675	—	10	—	—
Australia	20271	407	146	—	—
France	15465	6830	3335	202	32
Germany	28571	9078	8629	71	—
Japan	462	1516	—	—	48
Great Britain	110714	10460	14174	441	60
British India	658	130	106	—	—
Dutch Indies	100	100	—	—	—
Norway	600	—	—	—	—
Holland	6485	2125	4188	—	—
Rumania	—	77	50	58	—
U. S. A.	239317	16364	31049	—	—
Sweden	645	545	285	—	—
Spain	2728	810	158	—	—
Switzerland	211	—	—	—	—
Uruguay	455	130	90	—	—
Czecho-Slovakia	524	100	278	—	—
Turkey	—	112	—	—	—
Bulgaria	25	—	—	—	—
Portugal	120	—	—	—	—
British South Africa	300	—	—	—	—
Greece	210	22	53	—	10
Total kilos net	438821	50880	63500	772	210

Altogether kilos net 554183.—

against „ „ 569744.— in 1920.

[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 604.

These exports were distributed over the various months as specified hereafter: —

		1920	1921
January . . . . . kos gross		98851.—	66865.—
February . . . . „ „		81735.—	173851.—
March . . . . . „ „		102096.—	105497.—
April . . : . . „ „		67280.—	108987.—
May . . . . . „ „		50533.—	70009.—
June , ... „ „		53348.—	85988:—
July . . . . . „ „		53102.—	48397.—
August . . . . „ „		41332.—	27310.—
September . . . ჳ „		45015.—	49214.—
October . . . . „ „		76721.—	51198.—
November . . . ჼ „		142904.—	44691.—
December . . . „ „		133133.—	72868.—
kos gross		946050.— 1)	904875.— 1)

Average prices in 1921.

The prices are understood in Italian Lire for 1 Sicilian pound of 317 grams.

Month			Lemon oil	Bergamot oil	Orange oil, sweet	Orange oil, bitter	Mandarin oil
January:	3rd to	8th	11.75	82.—	46.—	35.—	100.—
„	10th „	15th	11.75	81.—	46.—	34.—	95.—
„	17th „	22nd	11.—	80.—	45.—	32.—	95.—
„	24th „	31st	10.—	79.—	44.—	31.—	93.—
February:	1st „	5th	9.50	77.—	43.—	32.—	90.—
„	7th „	12th	9.50	77.—	43.—	32.—	85.—
„	14th „	19th	9.50	77.—	43.—	32.—	85.—
„	21st „	26th	9.25	75.—	42.50	31.—	83.—
March:	1st „	5th	8.50	73.—	41.—	30.—	80.—
„	7th „	12th	8.50	72.—	40.—	28.—	78.—
„	14th „	19th	8.50	70.—	40.—	28.—	78.—
„	21st „	31st	8.25	69.—	40.—	28.—	78.—
April:	2nd „	9th	7.—	66.50	34.—	24.—	70.—
„	11th „	16th	6.50	68.—	34.—	23.—	67.—
„	18th „	23rd	6.—	68.—	33.—	23.—	55.—
„	25th „	30th	5.75	66.—	33.—	23.—	55.—
May:	2nd „	7th	5.50	64.—	31.50	22.—	50.—
„	9th „	14th	5.25	62.—	31.—	22.—	50.—
„	16th „	21st	5.25	60.—	30.—	21.—	45.—
„	23rd „	31st	5.50	58.—	28.—	20.—	45.—
une:	1st „	4th	5.80	50.—	23.—	17.—	40.—
„	6th „	11th	5.80	50.—	20.—	17.—	45.—
„	13th „	18th	6.—	54.—	—	—	45.—
„	18th „	30th	7.—	55.—	—	26.—	50.—

1) The net weight is arrived at by deducting 40 per cent.

Month			Lemon oil	Bergamot oil	Orange oil, sweet	Orange oil, bitter	Mandarin oil
July:	1st „	9th	7.75	55.—	34.—	26.—	50.—
„	11th „	16th	7.75	53.—	32.—	26.—	50.—
„	18th „	23rd	7.25	53.—	31.—	27.—	59.—
„	25th „	30th	7.75	55.50	35.—	28.—	62:—
August:	1st „	6th	8.50 to 11.—	60.— to 68.—	38.50	30.—	65.—
„	8th „	13th	10.50	78.—	43.—	32.—	70.—
„	16th „	20th	9.75 to 11.—	78.—	47.—	33.—	75.—
„	22nd „	30th	10.—	74.—	47.—	49.—	85.—
September:	1st „	10th	9.75	73.50	46.—	48.—	83.—
„	12th „	17th	9.25	72.—	45.—	46.—	83.—
„	19th „	24th	8.80	71.—	43.—	48.—	83.—
„	26th „	30th	8.75	70.50	41.25	50.—	78.—
October:	1st „	8th	8.50	70.—	40.—	45.—	76.—
„	10th „	15th	8.30	78.—	39.—	41.—	74.—
„	17th „	22nd	7.75	70.—	38.—	37.—	75.—
„	24th „	29th	7.50	70.—	39.—	34.—	72.—
November:	2nd „	5th	8.—	70.—	42.—	33.—	71.—
„	7th „	12th	8.—	68.—	43.—	34.—	70.—
„	14th „	19th	7.75	67.—	41.—	34.—	70.—
„	21st „	26th	7.50	63.—	40.—	34.—	65.—
„	28th „	30th	7.—	61.50	39.—	33.50	65.—
December:	1st „	3rd	7.—	61.—	38.—	33.50	60.—
„	5th „	10th	7.—	60.50	38.—	34.—	60.—
„	12th „	17th	7.50	60.—	38.—	34.—	55.—
„	19th „	24th	8.—	59.75	37.50	32.—	55.—
„	26th „	31st	8.50	60.—	37.—	31.—	55.—

Bergamot Oil. — After a short period of comparative firmness towards the end of April last year, the market relapsed into the old dull state, so that the prices sank nearly 20 per cent. Attempts made from certain quarters to monopolize the market, failed. Only in the course of the month of August, a sudden change took place, owing to a vivid demand from all foreign countries, which coincided with the purchases speculators had to make in order to cover their engagements. However, there was a noticeable downward tendency again already in the following two months, as the coming new crop induced various producers to put their stocks on the market. The yield of last year's autumn pressing is somewhat lower than the previous one, but in consequence of lack of transactions the position of the article continues weak. One may therefore reckon with further declining prices.

A. Parozzani[1]) investigated bergamot oils of the 1921/22 Calabrian crop. Whereas the oils of the previous year were conspicuous by their high optical rotation, low

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[1]) *Annali della R. Stazione Sperimentale per l'industria delle essenze e dei derivati dagli agrumi* 2 (1922), 1. According to a reprint kindly sent us.

, ester content and defective solubility, most of the products now dealt with showed almost normal constants: The specific gravity is generally in proportion with the ester content (there are no exact indications), $\alpha + 12$ to $+22°$ (on an average $+16$ to $+17°$), soluble in 80 and 82.5 per cent. alcohol, ester content 31 to 36 per cent. for the oil prepared in November/December and 36 to 39 per cent. for that obtained in January/February. In some regions, the optical rotation of the oils was $\alpha + 28$ to $31°$.

It results from these constants, as the author remarks, that the effects of the drought in summer 1920 is less noticeable in the quality of this year's product than in that of last year's crop, but there is not a similar improvement in the yield. The quantity expected is only 70 to 75000 kilos, i. e. less than half a normal crop.

With regard to the remarks which we connected with our discussion of Parrozani's publication on bergamot oil of the 1920/21 crop (our last *Bericht*, p. 20), the author points out that the constants established by him do not refer to the oils from fallings but to those of ripe fruits. He further states that the samples have always been collected by officials of the stations in the various producing districts, who also watched the manufacturing process. The high rotatory power of the oils (α up to $+37°$) was easily explained by that of the terpenes contained therein (α up to $+72°$). There could not be any suspicion of adulteration with lemon or orange oils. Besides, his figures were not intended to be a firm criterion for bergamot oils, but meant to show that absolutely pure oils may sometimes have abnormal constants.

Lemon Oil.—The downward tendency, of which we reported a year ago, lasted until May, when such a low price level was reached that all concerned in the lemon oil trade had to sustain the most serious losses. A fairly brisk demand which then arose, sent the prices up a little, but only for a very short time, as the rumours of bad prospects for the next crop proved to be exaggerated. Even a vivid demand, especially from the United States, in the course of September, only led to a very moderate hardening of the market, and although the October shipments were twice as large as those of the previous month, no considerable rise was caused, as the imminent new crop induced the producers to come forth with their stocks. The yield was normal and taking into consideration the quantities still available of the old crop, it is thought that a further decline of the prices may be predicted, as speculative attempts to bring about a change have always only had a temporary effect. Only if the chief places of consumption showed a much keener interest in the article, conditions might alter.

Sicily supplies 88 per cent. of the total Italian lemon crop, whereas Calabria only contributes 4, Campania 3.5, Apulia and Liguria 2 each and Sardinia 0.5 per cent.[1]). Most of the fruits are exported, only part being used for the manufacture of the essential oil. In Palermo 90 per cent., in Siracusa 60 per cent. and in Catania 40 per cent. of all the Citrus trees grown are lemon trees. The varieties cultivated most are those producing oval fruits with a thin and smooth skin. Good lemons are supposed to have pale yellow skin without any excrescences, sour juice and few pippins. In Sicily, the following classification is made according to the time of gathering: — A) *Marzioli* or *Massani*. They ripen in December, provided that favourable weather immediately after the normal crop, i. e. in March, produces another bloom. B) Lemons. They are the fruits of the normal bloom in April and May, ripening from December to February and being collected during these months. C) *Biancucci* or *Bianchetti*, also

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[1]) H. C. Holtz, *Chem. Weekblad* 18 (1921), 108.

called *Ricioppi*. These ripen after the normal crop and come from June blossoms. D) *Verdelli*. They are summer fruits, forced to premature ripening by a special process. The trees are left dry until the end of July, but then watered profusely. This causes an abundant bloom in August and September, so that the still greenish fruits can already be gathered in the following summer. Although this proceeding shortens the life of the trees from 80 to 40 or 50 years, the yield of *Verdelli* offers ample compensation for this disadvantage. E) *Bastardi* or *Bastardoni*. These are the names of the belated fruits of the *Verdelli* crop, gathered in August. It is said that the rotatory power of the oil from *Bastardoni* and *Bianchetti* is not higher than 54°[1]).

For the manufacture of the essential oil, only such lemons are used, the abnormal size or form or other undesirable qualities of which make them unfit for being exported. These rejected fruits amount to about 25 per cent. in the Palermo and Siracusa districts, whereas in those of Messina and Catania they may come up sometimes to 75 or even 80 per cent. of the crop.

According to De Salvo, 63000 lemons yield 100 Sicilian pounds $=$ 32 kilos of oil. The same as with the bergamots, more and better oil is obtained from green than from ripe fruits. In consequence, the lemons gathered from December to February are to be preferred. The lemons growing near the coast of Amalfi (Campania), for instance, which ripen very late (in summer), contain so little oil that is does not pay to obtain it.

Messina is the most important Sicilian export harbour for lemon oil, although a certain part goes from Catania and Siracusa. Reggio is the centre for the oils produced in Calabria.

Of the various methods of determining the citral content, Holtz considers to be the best those of Walter and Bennett (with hydroxylamine)[2]), Kleber (with phenylhydrazine) and Romeo (with neutral and acid sodium sulphite). The last-named method, by means of which according to Berté and Patané[3]) a citral content of 4 to 5.6 per cent. is found for good lemon oils, is used in the laboratory of the Messina Chamber of Commerce. Patané thinks[4]) that far too much value is attached in commerce to the citral content, which ought not to be less than 4 per cent.[5]). The aroma of the oil depends on other constituents, present in small quantities and which do not come into consideration for the usual chemical analysis. The lemon oils of the finest aroma, *i. e.* those of the November/December crop, contain less citral than the inferior qualities of February/March.

Orange Oil, bitter. — The lowest price level was reached towards the middle of June, with 17 Lire, until in the middle of July the general rise of all the citrus oils also affected this article. The climax was 50 Lire, end of September, but already in October the price had gone down again to 34 Lire. The new crop is satisfactory, and as there are old stocks from 1920 one may reckon with a continued feeble tendency for the next months.

Orange Oil, sweet. — The price, which in March 1921 was still 40 Lire, sank to one half of it towards the middle of June, hardened gradually during the months of July and August, reaching its highest stage end of the latter month at about 47 Lire.

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[1]) According to other observations, $+54°$ is the lowest limit, down to which the optical rotation may go. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 17. — [2]) In our opinion this method is to be preferred, although the figures arrived at are 10 per cent. too low, referred to the amount of citral present. Comp. *Report* October 1909, 154. — [3]) *Riv. Ital. Essenze e Prof.* 1919, I., p. 7 and 30. — [4]) *Id.* p. 7. — [5]) Comp. *Report* April 1914, 58.

This rise was chiefly due to the vivid demand from abroad, but it was accentuated by the supposition that the lasting rain would seriously damage the blossom. Besides, speculative purchases were made to a very great extent, with a view to force the article into an upward movement. This scheme did not succeed, however, owing to the buyers' refusal to pay the high prices demanded and to the approaching new crop. A firmer tendency, noticed in March, was only temporary, and at present the article is rather neglected, the same as the other Citrus oils.

According to official statistics[1]), the Italian orange crop originated as follows:— Sicily 57 per cent., Calabria 20 per cent., Campania 16 per cent., Apulia 3 per cent., Liguria 0.7 per cent., other districts 3.3 per cent. Only second-rate fruits are used for manufacturing the oil, 70000 oranges being required for producing 100 Sicilian pounds, equal to about 70 English pounds. According to the statistics of the Exchequer, the exports of bitter and sweet orange oils were as follows:—

1917	. . . .	72347 k°ˢ	to the value of	2532145 Lire
1918	. . . .	49109 „	„ „ „	„ 1964360 „
1919	. . . .	103913 „	„ „ „	„ 4156520 „

France, the United States and England were the principal importers.

In 1919, Jamaica exported 168415 lbs. of orange oil. According to an English periodical[2]), this large shipment was due to the exceptionally good price obtainable for the oil. Jamaica's capacity for orange production is nearly a million boxes at present. Within ten years this output might be doubled, if she could obtain a regular profitable market. But the prohibitive U. S. A. tariff against Jamaican fruit and restricted shipping to the United Kingdom held back orange cultivation. The Jamaica Agricultural Society is urging the Government of the Island to make further representations to the Canadian Government for a preferential duty on West Indian fruit. This the Canadian Government have so far declined to do, alleging that the British West Indies can only supply a small portion of the amount required. Jamaica replies that, given such encouragement, there would at once be a responsive effort in making her neglected trees more productive, and new plantations would be engaged in, for certain districts in the island have such conditions as make orange cultivation their best industry.

P. Mirgodin[3]) describes a so-called "new" machine, constructed by the "Ecuelles Ltd." and invented by two West Indian planters, with the aid of which the essential oil can be obtained from the various citrus fruits. He states that from 0.5 to 1 oz. of lemon oil and 2 to 3 ozs. of orange oil or oil of limes can be got from one bushel of fruits. The machine is constructed in three different sizes. It results from Mirgodin's description that the peeling process, described years ago by Hood and discussed by us[4]) is here referred to.

A disease which occurs in most citrus-growing countries and is fairly prevalent in Australia, the so-called collar rot[5]), often escapes the notice of the growers until serious damage has been done. Its appearance and treatment are described in Agric. Gaz., New South Wales (1920, 31, 439). Collar rot manifests itself most frequently by "gumming" on the trunk just above or close to the ground. In many cases the bark in the vicinity is dry and brittle. In young trees the leaves show "yellowing", or chlorosis, especially on terminal twigs, but in older trees chlorosis may not develop

¹) H. C. Holtz, *Chem. Weekblad* 18 (1921), 108. — ²) *Perfum. Record* 12 (1921), 184. — ³) *Parfum. moderne* 14 (1921), 257. — ⁴) Comp. *Bericht* (German) 1920, 32. — ⁵) *Bull. Imp. Inst.* 18 (1920), 437.

until the attack has reached an advanced stage, when the tree has been nearly ring-barked. Associated with the disease[1]), a fungus parasite *(Fusarium limonis)* is constantly found, which enters the tree at an injured part, goes very slowly through the tissues of the trunk, and if left unchecked accomplishes the ring-barking of the tree. The treatment recommended when "gumming" has been observed is to scrape the earth away from the base of the tree, remove the dried bark apparently infected by the fungus, and paint the wound with a bluestone paste composed of $1^1/_2$ lbs. of copper sulphate, 4 lbs. of unslaked lime and $1^1/_2$ gallons of water. Where collar rot is too far advanced for the tree to be saved by this treatment it should be removed and burned, and the stump-hole limed. Bad drainage is conducive to this disease.

Estragon Root Oil. — Estragon roots, collected in Miltitz, yielded on distillation with steam 0.21 per cent. of a dark brown oil. The feeble smell recalled somewhat that of radishes and was, in any case, entirely different from that of the herb: — d_{15^0} 0.9744, n_{D20^0} 1.56406, acid v. 2.1, ester v. 14.4, soluble in 5 vols of 90 per cent. alcohol with turbidity, which gradually diminishes on further dilution. Owing to the dark colour, it was impossible to determine the optical rotation.

Eucalyptus Oil. — As per an American report[2]), the eucalyptus oil industry in Victoria appears to be in a very low condition, many of the distillers having ceased to work. In the Maryborough district, only one distillery is at work. In the Neilborough district, about half the factories are working, but only at low-grade oils.

In a communication dealing with piperitone, J. Read and H. G. Smith[3]) furnish some details concerning the history of the "peppermint" eucalypts of Australia.

Soon after the arrival of Governor Phillip in New South Wales, in 1788, a species of this peppermint type, growing plentifully in the neighbourhood of Port Jackson attracted the attention of the colonists, and the first eucalyptus oil to be distilled was obtained from its foliage and employed for medicinal purposes by Surgeon-General Dr. White, who gave the plant the name Peppermint Tree on account of the very great resemblance between the essential oil drawn from its leaves and that obtained from the peppermint in England. The oil was found by Dr. White to be much more efficacious in removing all cholicky complaints than the English peppermint oil. Nowadays, the tree is known to have been *Eucalyptus piperita*, which is common in the Sydney district and the Blue Mountain Ranges of New South Wales[4]).

The eucalypts of the "peppermint" group are now known[5]) to contain piperitone $C_{10}H_{16}O$ (*p*-menthenone-3), occurring, with the exception of *E. apiculata*, in association with l, α-phellandrene and, in most cases, also with the corresponding secondary alcohol piperitol. When isolated in the usual way, by fractional distillation under atmospheric pressure followed by treatment with sodium hydrogen sulphite solution, the piperitone, on regeneration, undergoes racemisation and usually exhibits a feeble laevoratation not exceeding $[\alpha] - 1^0$. Read and Smith ascribe this to the possible presence of small quantities of the laevorotatory aldehyde "cryptal". By conducting the distillations,

[1]) According to the description the so-called "gumming" disease *(gummosis)*, which may attack all sorts of citrus-trees, seems to be referred to. Comp. *Bericht* (German) 1921, 89. — [2]) *Americ. Perfum.* 16 (1922), 318. — [3]) *Journ. chem. Soc.* 117 (1921), 779. — [4]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 277. — [5]) *Ibidem*, p. 283.

however, under greatly diminished pressure it is possible to isolate the piperitone in its natural, markedly lævorotatory form ($[\alpha]_D - 42.8°$)[1]).

A specimen of piperitone obtained by Read and Smith from the essential oil of *Eucalyptus dives* by distillation under atmospheric pressure and by purification by means of neutral sodium sulphite, showed the constants: — b. p. 128.5° (25 mm.), $[\alpha]_D - 0.27°$, $n_{D20°}$ 1.4843; hydroxylamino-oxime, m. p. 169 to 170°; oxime, m. p. 110 to 111°; semicarbazone, m. p. 219 to 220°. (The semicarbazone prepared by Wallach[2]) from Δ^1-*p*-menthenone-3 had the m. p. 224 to 226°.) On treating piperitone with benz-aldehyde in presence of metallic sodium the authors obtained benzylidene-*d,l*-piperitone $C_{10}H_{14}O : CH \cdot C_6H_5$, m. p. 61°; oxime, m. p. 130 to 131°.

The bimolecular ketone $C_{20}H_{34}O_2$ from piperitone obtained by Baker and Smith, under the identical conditions, yielded no benzylidene compound.

From the oil of *Eucalyptus hemiphloia*, R. T. Baker and H. G. Smith[3]) succeeded in obtaining a new crystallised phenol which they termed *australol*. This phenol, which occurs also in other oils of the "Boxes", was prepared in the same manner as tasmanol (comp. *Report* 1916, 30) and showed the following constants: — m. p. 62°, b. p. 115 to 116° (10 mm.), $d_{20°}$ 0.9971, $\alpha_D \pm 0$, $n_{D20°}$ 1.5195, mol. refr. found 41.50; calculated for three double bonds 41.74; benzoate, m. p. 72 to 73°. In alcoholic solution, ferric
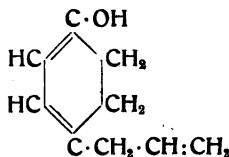
Probable structure of australol.

chloride gave with the phenol a fleeting greenish yellow colour at first, quickly changing to bright yellow. The odour of australol reminded of ordinary phenol, and the skin was attacked by the new phenol in exactly the same manner as by phenol. Combustion and molecular weight determination proved the empirical formula $C_9H_{12}O$. Since the unsaturated phenol gave no colour reaction with picric acid, the unsaturated side-chain has most probably the allyl grouping, two double bonds thus occurring in the nucleus. The authors conclude, therefore, that australol is a dihydro-*p*-allylphenol of the structure given above.

From the oil of *Eucalyptus hemiphloia* and related eucalypts, Baker and Smith obtained formerly[4]) an aldehydic body which they termed aromadendral. Recently[5]) it was found that this body, which occurs likewise in the oils of the "Box" and "Mallee" group, was no uniform substance, but a mixture of aromadendral proper, $C_{10}H_{14}O$, with cuminal $C_{10}H_{12}O$, phellandral $C_{10}H_{16}O$ and a new aldehyde "cryptal" $C_{10}H_{16}O$. The latter aldehyde had escaped the authors in their first investigation, because it did not form a solid compound with sodium bisulphite, and the liquid combination is not decomposed by sodium carbonate. These very properties afforded later on a satis-factory method for the preparation of the new aldehyde. According to a method given in detail, the authors succeeded in isolating, as they believe, pure cryptal from the oils of *Eucalyptus hemiphloia* and *E. polybractea*. However, the constants of both aldehydes do not agree with each other[6]).

Cryptal from the oil of *E. hemiphloia*: — b. p. 99 to 100° (10 mm.), 221° (760 mm.), $d_{20°}$ 0.9431, $\alpha_D - 76.02°$, $n_{D20°}$ 1.4830; semicarbazone m. p. 176 to 177°; oxime and hydrazone were liquid.

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[1]) Comp. *Bericht* 1921, 24. — [2]) *Liebig's Annalen* 362 (1908), 272. — [3]) Baker and Smith, *A Research on the Eucalypts and Their Essential Oils*, 2nd edition 1920, p. 396. — [4]) Comp. *Reports* April 1901, 34; October 1901, 29. — [5]) Baker and Smith, *A Research on the Eucalypts and Their Essential Oils*, 2nd edition, 1920, p. 383. — [6]) No explanation is given for this discrepancy.

Cryptal from the oil of *E. polybractea:* — d_{200} 0.9443, α_D — 49.7°, n_{D200} 1.4849; semi-carbazone, m. p. 180°; oxime and hydrazone were liquid.

Attempts to separate aromadendral $C_{10}H_{14}O$ from the other aldehydes present in the oil in the pure state, were hitherto without success, cuminal being mostly present.

Oil of the Bark of Eucalyptus Macarthuri. — From the ground bark of *E. Macarthuri,* Deane et Maiden, a species cultivated on a large scale near Emerald, Victoria, Baker and Smith[1] obtained by steam-distillation 0.12 per cent. oil of a light amber colour and a distinct odour of geranyl acetate. Three different samples of this oil showed the following constants: — d_{150} 0.9099 to 0.9218, α_D + 1.2 to + 1.4°, n_{D200} 1.4648 to 1.4718, soluble in 1.2 vols. of 70 per cent. alcohol, ester v. 169.5 to 195, equal to 59.2 to 68.2 per cent. geranyl acetate; ester v. after acet. 198.8 to 224, equal to 69.6 to 78.4 per cent. ester.

The optical rotation of the oil is ascribed to the presence of a small quantity of *d*-pinene. Eudesmol, a constant constituent of the leaf oil from *Eucalyptus Macarthuri,* does not appear to be present in the bark oil. Apart from this, the constants of both oils appear to be fairly identical.

Fennel Oil. — Our industry has not seen much of the good yield of last fennel crop, as the largest share by far was sent abroad, where higher prices were obtainable. Even the factories situated in the vicinity of Lützen fennel districts did not succeed in buying fair quantities. It would have been better if the Government had taken the suggested measures for stopping the export, or at least restrict it, so that the work connected with the distillation of the fennel seeds remained in the country. It is to be hoped that something will be done with regard to the next crop, as otherwise the distillation of fennel oil will pass entirely out of the hands of the German industry.

C. E. Sage[2] examined two fennel oils of Spanish origin and known to have been prepared from the entire plant of *Fœniculum vulgare.* The following constants, found by him, seem to indicate that the products in question were at least partly composed of bitter fennel oil: — $d_{15.50}$ 0.9203, and 0.9340, α_D + 46° and + 24°, n_{D250} 1.4945 and 1.4980, soluble in 1 vol. of 90 per cent. alcohol, congealing point ... no indication at — 15°.

Frankincense Oil. — By fractionated distillation of 1 kilo of terpeneless oil of frankincense[3] in a vacuum, E. Fromm and R. Klein[4] obtained a body $C_{10}H_{16}O$, b. p. 117 to 119° (22 mm.), 210 to 211° (ordinary pressure), d_{180} 0.9504. This compound, called α-olibanol by the authors, was not identical with the olibanol prepared by Fromm and Autin[5], also from oil of frankincense, as it did not yield any pinonic acid on oxidation with potassium permanganate. The olibanol that yielded pinonic acid could be obtained, however, if the oil of frankincense or the product of the distillation were distilled under ordinary pressure. There are in consequence two olibanols; *viz.,* α-olibanol, as found in the natural oil of frankincense, and β-olibanol, formed through a re-arrangement of the molecules on heating the former above its boiling point. As α-olibanol does not yield any pinonic acid, it is neither identical with verbenol, nor with dihydroverbenone. On reducing α-olibanol with sodium and alcohol, dihydro-olibanol is formed, $C_{10}H_{18}O$ (b. p. 100 to 102° [25 mm.], *o*-nitrobenzoate, m. p. 135 to 137°), which is not identical with dihydro-verbenol.

[1] *A Research on the Eucalypts and Their Essential Oils,* 2nd edition 1920, p. 318. — [2] *Perfum. Record* 12 (1921), 46. — [3] Cf. page 142 of this *Report.* — [4] *Liebigs Annalen* 425 (1921), 213. — [5] Cf. *Report* April 1914, 63.

When trying to reduce the β-olibanol in the same way, the authors only obtained the unaltered material, in addition to resinous products.

An ordinary oil of frankincense, distilled *in vacuo*, yielded a compound $C_{10}H_{16}O$ (b. p. 114 to 116° [15 mm.], $d_{18°}$ 0.9502). This product (γ-olibanol) which it was impossible to reduce like α-olibanol or to transform into the β-compound by heating, yielded on oxidation a liquid acid and did not react with semicarbazide. Even after ordinary oil of frankincense had been stored for five years, no α-olibanol had formed in it.

Geranium Oil. — The production of geranium oil in North Africa has decreased considerably. Whereas 140000 kilos were distilled in Morocco, Algiers and Tunis, in 1914, only 15000 kilos were obtained in these three countries in 1920. In consequence, the price rose from 30 or 35 Francs in 1914 to 250 Francs per kilo in 1920. There was a change, however, in 1921, for in spite of a very small crop (only 14000 kilos) not more than 70 Francs were paid per kilo in the producing districts. As the geranium growers find these low prices unprofitable, they intend giving up the cultivation of the geranium plant altogether[1]).

A. Rolet[2]) reports on the crops and the yield of geranium plants in various countries, where the plant is cultivated. The time of the crop varies according to the district and the way of cultivating. In the Provence, the crop takes place in August/September, very rarely for a second time in October/November. As the plants would freeze in winter, a fresh cultivation must be started every year. As soon as the leaves lose their lustre, the plants are mown, preferably towards evening on fine days, so that the herb does not dry out too much.

In Corsica *(Pelargonium odoratissimum)*, there are two cuts, in May and August, very seldom a third one in September/October, when only slips come into consideration[3]).

In Algiers, the crop begins already in spring, generally in April, as soon as the plants start flowering. There is a second cut in June/July and a third one in October-November. There are five crops within two years, the yield being smaller in the first year than later on. On good soil, such as in Boufarik, the stalks are from 50 to 70 cm. long, otherwise they only measure from 25 to 30 cm.[4])

In Italy *(Pelargonium roseum,* Willd.), there is only one crop in the first year of cultivation, in August/September, whereas in the second year the plants are cut in May, August and October/November. The plants can be used there for four, sometimes even for up to eight years. If only the flowers are gathered, the oil of which is supposed to be finer, according to Blandini[5]), the crops are more frequent. The author once started on the 18th of April in Portici and left off gathering the flowers on June 14th, after having had eight crops.

In Réunion, one crop follows the other[6]). If the intention is to keep up the cultivation for several years, the plants are cut down more than if they are renewed every year. In order not to uproot the plants, tree-shears are used for cutting in the first year and sickles later on. The cut plants are sent at once to be distilled, for if they stay in heaps for some time they get hot, start fermenting and lose in value.

The output varies and depends on all sorts of circumstances, such as way of cultivating, soil, manure, irrigation, number of crops, &c.

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[1]) *Zeitschr. d. Deutsch. Öl- u. Fett-Ind.* **41** (1921), 825. — [2]) *Parfum. moderne* **13** (1920), 60. — [3]) Comp. *Report* October 1910, 70. — [4]) Comp. *Report* October 1913, 61. — [5]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 614, foot-note 5. *Report* April 1907, 54. — [6]) Comp. *Report* April 1914, 64.

In the Alpes Maritimes in France, from 25 to 80000 kilos (on an average 40000 kilos) per hectare and year can be obtained on well irrigated, artificially manured soil, if great care is taken of the plants. In the Var department, the yield may come up to 75 and even 100000 kilos per hectare, according to L. Robertet.

In Algeria the crops are estimated at from 25 to 27000 kilos per hectare.

Blandini obtained from *Pelargonium roseum*, Willd., in Italy 26000 kilos of herb and 3945 kilos of flowers per hectare.

R. Knuth[1]) has published an extensive article on geranium oil (botany, distribution, cultivation and yield of the mother-plant and its varieties, chemistry of the oil and its components), with several good pictures of *Pelargonium* species. The author thinks that the plants cultivated in the various countries may be considered either as varieties of cultivation or hybrids of other species, whose origin is now unknown or has been forgotten long since. In the beginning of the nineteenth century, there was a sort of fad to hybridize *Pelargonium* species, so that, for instance, the *Geraniaceæ* of Sweet[2]) (London 1820—1830) contain almost 500 of such artificial hybrids, whose origin already at that time had been partly unknown. In the course of time, the origin of each cross became more and more obscure, so that at the present time we are unable to determine te exact origin of a large part of the pelargoniums found in our botanical gardens. This is especially the case with regard to the species which were called lemon-geraniums as early as the time of Sweet, and with which the rose-geranium must be included[3]).

Andrews[4]), in his *Geraniums* (1805), mentions a *Pelargonium oxoniense*[5]), closely related to *Pelargonium graveolens* and *Pelargonium capitatum*, which was first cultivated in Oxford on account of its rose-odour and sold under the name of *Oxoniense roseum*. Knuth thinks it very probable that the parent plant of the rose-geranium was originally purchased under the name of *Oxoniense roseum* and is related to *Pelargonium oxoniense*. Heuzé[6]) and Cordemoy[7]) are mistaken in thinking that the species chiefly cultivated in Algeria and Réunion is *Pelargonium capitatum*, as the plant found there has leaves entirely different in shape from those of *P. capitatum*. This species rather belongs to the group of *Pelargonium graveolens*, L'Hérit.

It is probable that in France, in addition to rose-geranium, *Pelargonium odoratissimum* (L.), Ait. (belonging to the section of *Peristera*, according to Harvey) and *Pelargonium fragrans*, Willd. (a hybrid of *Pelargonium odoratissimum* and *P. exstipulatum*, L'Hérit.) are cultivated, though to a smaller extent. Both plants have a delicate texture and differ also in other ways from the rose-pelargonium. In Algeria and Réunion the two species are certainly not cultivated.

The oil is furnished by the glands of the plant. These are found, as in all pelargonium species, in the green parts, especially on the surface of the leaves, where they are shorter than on the stem and the peduncles. In most cases they are from $1/18$ to $1/15$ mm. long and can be seen with the naked eye. They consist of from one to three small cylindrical base cells and a small globular head, in which latter the oil is generally to be found When young, the end cell is colourless, later on it is coloured by a yellow substance and finally becomes brown. The oil glands are of great use to the plant, as they protect it against insects and snails. As a matter of fact, all pelargoniums are but little damaged by such enemies.

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[1]) *Americ. Journ. Pharm.* 93 (1921), 302. — [2]) Died as a market-gardener in London. — [3]) Knuth calls "rose-geranium" the chief parent plant of geranium oil. See lower down. — [4]) Herbalist in London, who published precious copper plates of foreign plants. — [5]) *Pelargonium oxoniense*, van Eeden (*Index Kewensis*). — [6]) *Revue Horticole* 65 (1893), 305. — [7]) *Revue Cult. Colon.* 1904, 170.

Blandini's assertion[1]) that the *flowers* produce a larger quantity of oil of excellent quality is in Knuth's opinion certainly not in accordance with the facts.

As to the geographical distribution of the plant, the author gives the following summary, many facts of which will be known already from our previous *Reports.* In France the plant was first cultivated near Grasse and at the foot of the Maritime Alps, near Cannes. Though it was known there as early as 1819, it seems to have been grown only to a limited extent up to 1847. Shortly after that time, emigrants transmitted the cultivation to Algeria, where the plant was first grown in the district of Sahel, Western Algeria, between Oran and Mostaganem, afterwards in the plain of Metidja, near Algiers, and in the littoral of the province of Constantine, near Philippeville and Bougie. The cultivation did not spread to Réunion before 1880. It was favoured there by the sugar crisis of 1904—1906. — In the Spanish province of Granada, experiments regarding the cultivation of the plant were made about 1890. Although the quality of the oil was excellent, the area of cultivation, producing from 600 to 1000 kilos annually, was not increased. — In the Jewish colonies of Asia Minor, Rischon-le-Zion and Petach-Tikway, there are plantations which were founded by Baron Rothschild. — The trial plantations of *Pelargonium radula* in Limaru, British East Africa, have not been continued. — The author states that he has not been able to obtain information concerning the cultivation of the plant in Córsica. We would mention that it was introduced there from the Provence, about 1860, and quickly spread in the districts of Erbalunga, Sisco and Brando.

We have reported repeatedly on adulterations of geranium oil with citronella oil or fractions thereof[2]). It is often difficult to recognize such admixtures, as the constants are not always influenced sufficiently to become abnormal. Under these circumstances, a careful examination of the smell will rouse suspicion, but only an exact chemical analysis can give absolute certainly.

We had to deal with such a case quite recently, when a geranium oil was sent us for inspection from Spain. It behaved as follows: — $d_{15°}$ 0.9002, α_D — $6°38'$, $n_{D20°}$ 1.47171, acid v. 5.2, ester v. 50.8 = 21.4 per cent. ester, calculated as geranyl tiglinate, ester v. after acetylation 213.7 = 70 per cent. total geraniol, soluble in 2.3 vols. and more of 70 per cent. alcohol, dilute solution slightly turbid. As the product was supposed to be a Bourbon oil, it struck us that the constants were abnormal in part, the specific gravity and the index of refraction being too high, the optical rotation too low. The sample therefore resembled rather an African distillate, but was suspicious in any case on account of its odour and defective solubility. It was proved through investigation that the oil contained an appreciable quantity of citronellal, a substance which is not a component of geranium oil. With the aid of bisulphite, several grams of citronellal were isolated out of 125 grams of the oil under examination and identified by means of the semicarbazone, melting between 82 and 83°. A mixture with a semicarbazone prepared for the sake of comparison showed the same melting point, so that the identity of the two compounds is certain.

In order to make quite sure, we treated 125 grams each of genuine pure Bourbon and African geranium oils in the same way with sodium bisulphite, when the quantities of aldehydic components obtained were so small that a chemical identification resulted impossible, whereas the smell seemed to indicate citral or a fatty aldehyde rather than citronellal.

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[1]) *Bull. de l'Off. du Gouv. de l'Algérie* 12 (1906), 277. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 614, foot-note 5. — [2]) Comp. *Report* 1917, 19 and *Bericht* (German) 1920, 36.

On account of this result there can be no doubt that we had to deal with an adulteration. We presume that there was an admixture of citronella oil or a fraction thereof, which would explain the defective solubility.

Gingergrass Oil. — Two samples, described as sofia oil, were forwarded to the Imperial Institute from Dehra Dun in 1916. On investigation[1]), the oils revealed the following constants: — $d_{15^\circ}^{15^\circ}$ 0.910 and 0.907; α_D —15° 48' and —14° 3'; sol. in 2.1 and 2.0 vols. of 70 per cent. alcohol, no opalescence on dilution to 10 vols.; acid v. 2.3 and 1.5; ester v. 25.7 and 19.8; ester v. after acet. 170.5 and 180.6. The oils showed a slight odour of citral, the absorption test with sodium hydrogen sulphite, however, manifested nothing abnormal in this respect, since the two oils contained 12 and 11 per cent. of matter soluble in that reagent, whereas of a commercial oil 10 per cent. were absorbed.

A further sample of the same oil originating from the United Provinces of India (1917) had the constants: — $d_{15^\circ}^{15^\circ}$ 0.936; α_D +42.87°; n_{D20° 1.490; insol. in 70 per cent. alcohol; acid v. 4.5; ester v. 13.5; total alcohols, calculated as geraniol, 42.7 per cent.

Oil of the Berries of Heeria paniculosa. — The berries of this anacardiacea[2]), indigenous in Zululand and known there as *isifeku,* yielded on water-and-steam-distillation 4.47 to 6.07 per cent. essential oil[3]). The oil is located especially in the pericarp and shows no particular odour. It consisted for the greater part of terpenes and had the following constants:—d 0.832, α 3.75°[4]), acid v. 1.6, ester v. 4.2, ester v. after acet. 14.8.

Oil of Houttuynia cordata.—By steam distillation of the herb *Houttuynia cordata,* Thunb., a piperacea known as *Dokudame* in Japan, Y. Shinosaki[5]) obtained 0.0049 per cent. of a light brown essential oil with a strong, somewhat disagreeable odour, and the following characters: — d_{15° 0.8744; $[\alpha]_D$ —5°; n_{D20° 1.4685; acid v. 16.65; sap. v. 28.40. On treatment with sodium bisulphite, methyl *n*-nonyl ketone (semicarbazone, m. p. 122 to 123°) was isolated. Repeated distillation of the residual oil is yielded a terpene fraction, b. p. 60 to 61° (14 mm.), 167 to 168° (766 mm.), as the principal product; this consisted of an aliphatic terpene (probably myrcene) and a small quantity of a cyclic terpene. The oil also appears to contain a solid acid.

Oil of Juniperus taxifolia. — From the leaves and twigs of *Juniperus taxifolia,* Hook. et Arn. (Japanese *shimamuro*), a coniferous plant indigenous to the Ogasawara Islands, Y. Shinosaki[6]) obtained by distillation 0.24 per cent. of a light green oil. Two specimens of the oil had the following characters: — d_{15° 0.8675 and 0.8701; α_D —? and —29°; n_{D20° 1.4702 and 1.4718; acid v. 0.94 and 0.0; sap. v. 11.69 and 10.37; sap. v. after acet. 19.60 and 18.89. The oil contained above 50 per cent. of α-pinene (mainly *l,*α-pinene containing a small quantity of the *d,l*-α-isomeride) and possibly a bicyclic terpene, a free alcohol ($C_{10}H_{18}O$), ester, sesquiterpene, and sesquiterpene alcohol.

Oil of Juniperus thurifera. — According to L. Lestra[7]), there is only a difference in the size and the build of the fruits between *Juniperus thurifera,* var. *gallica,* De Coiny, growing wild in France, and *Juniperus thurifera,* L., occuring in Portugal, Spain and

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[1]) *Bull. Imp. Inst.* 18 (1921), 343. — [2]) This species is not mentioned in the *Index Kewensis* of 1910. — [3]) *Chem. News* 120 (1920), 277. Acc. to *Bull. Roure-Bertrand Fils,* April 1921, 135. — [4]) The direction of rotation is not quoted in the abstract. — [5]) *Journ. chem. Ind. Japan* 24 (1921), 557. *Journ. Soc. chem. Ind.* 40 (1921), A. 560. — [6]) *Journ. chem. Ind. Japan* 24 (1921), 202. *Journ. Soc. chem. Ind.* 40 (1921), A. 411. — [7]) *Parfum. moderne* 14 (1921), 210.

North Africa. The plant is also easily distinguished from other *Juniperus* species, like the very similar *Juniperus Sabina*, L., especially by the compactness and the shape of the sclerogen cells of the berries. After giving an exact botanical description of *Juniperus thurifera*, var. *gallica*, De Coiny, Lestra reports on the essential oil obtained by steam distillation of the various parts of the fresh plant. The yield amounted to 0.15 per cent. of a straw-coloured viscid oil (0.096 per cent. of the dry plant). The constants were as follows: — $d_{15°}$ 0.9115, $a_D + 32.2°$, $n_{D20°}$ 1.4963, soluble in chloroform and in 96 per cent. alcohol, in 20 parts of 70 per cent. alcohol, in 10 parts of ligroin (?), acid v. 6.5, sap. v. 67.4, ester v. 60.9 (ester content 21 per cent., in addition to 0.57 per cent. of free alcohol), iodine v. 24.5. Through experiments with animals, it was established that the oil is an emmenagogue, like oil of savin.

Lavender Oil. — When last year's crop began, the market was very weak, for in consequence of the sluggish sales a considerable part of the previous campaign (it is rumored even about half) was still unsold in the South of France. The prices offered to the gatherers were low in consequence, only 20 to 30 Francs per 100 kilos of flowers being paid, according to the district. It is to be taken into account that the usual daily wages amount to 15 or even 17 Francs and that one man cannot gather more than 70 to 80 kilos per day. No wonder that the gatherers restricted their work to the more easily accessible districts, *i. e.*, the lower regions. This may account for the fact that, according to the unanimous judgment of our informants, the ester content of the oils was somewhat lower, on an average, than in the previous year, for the qualities with a high percentage are distilled exclusively of flowers from high regions. Owing to the low collectors' wages, only half the crop, which was very good last year, is said to have been gathered. At first, good lavender oils only fetched from 55 to 60 Francs per kilo and there was very little demand. Only after the annual lavender oil fairs, the most important one of which took place at Digne on October 1st, the market became firmer, as some Grasse firms purchased considerable quantities. Business resulted more brisk early in December, due to a fair demand from abroad, and towards the middle of January about 100 Francs had to be paid for good qualities of 40 per cent. ester. Then there was a pause and the market is quiet now with a slight downward tendency. If nothing unforeseen happens and the demand continues slack, there may be a decline in the next months. However, it will scarcely be considerable, as a good many owners mean to keep back their production, being convinced that the rising costs of gathering, distilling, etc., will influence the coming crop and send prices up. Besides, there is the possibility of smaller crop this time.

According to a *Bulletin du Syndicat des Producteurs de Fleurs et d'Essence de Lavande du Département de Vaucluse et des Régions limitrophes*, published in March this year and dealing specially with the fair at Digne on October 1st 1921, the normal prices for lavender oils ought to be between 90 and 120 Francs, if it is taken into consideration that the pre-war figures for medium qualities ranged from 30 to 40 Francs per kilo. The author tries to prove that the costs have trebled and that the selling prices ought to go up in proportion. The costs of gathering (from 4 to 7 Francs per 100 kilos before the war) amounted to 25 Francs in 1919 and have sometimes exceeded 50 Francs in 1920. Last year, the manufacturers declared that, owing to the general depression and the sluggish sales, they would rather take no flowers at all than pay more than 10 to 12 Francs. The gatherers knew this and some of them were willing to work nevertheless, but they were few in number. The owners of the lavender districts wanted more hands, however, and could only get them through paying higher

wages. 25 Francs per 100 kilos had to be paid, but even then there were perhaps only 20 gatherers, where 200 were required. As the depopulation in the mountainous districts of Sault has reached about 20 per cent., as per the latest estimations, one will have to reckon with a shortage of labourers in the future.

The costs of keeping the lavender plants in good condition and those of transport of the flowers have likewise trebled. Up to 500 Francs have been paid for working 1 hectare of wild lavender with 4 animals, a price which is out of all proportion, but if one takes it that in some districts only $^1/_3$ hectare can be worked daily by two men with four animals, a cost of 150 to 200 Francs per hectare would seem justified. The wages of labourers and drivers and the cost of the fodder have risen from 7 to 25 and even 30 Francs in the mountains. The prices of the necessary implements have also trebled.

The same is the case with the costs of distillation and the general expenses. An ordinary still holding 300 litres cost before the war from 400 to 500 Francs, whereas already some time ago from 1200 to 1800 Francs had to be paid. Coal has risen from 50 to 500 Francs per ton plus 200 to 250 Francs for transport. The wages of the stokers have trebled and the amount of work done has gone down. Taxes and other expenses have risen too and there does not seem to be any chance of reduction.

Finally it is stated that, contrary to the estimation of last year's crop at 150000 kilos, the total turnover on all the different fairs had not even reached 100000 kilos and that there was very little oil left in the hands of the distillers.

A. Chiris[1]) reports, on the strength of his own investigations, on the differences presented by lavender oils obtained by open fire and by steam distillation. According to his ideas, the rotatory power of lavender oils distilled by open fire grows in absolute value with the ester contents. It is known[2]) that oils distilled by steam under otherwise similar conditions generally contain a higher percentage of esters than those obtained by open fire. Chiris points out that a high ester content is not always a criterion for the quality of the oil. Of two oils, one distilled by open fire and having 45.57 per cent. of esters, and the other oil, steam-distilled, having 52.65 per cent. of esters, he preferred the former, as being superior in aroma. As regards solubility and density, lavender oils distilled by steam are less soluble in 70 per cent. alcohol (not soluble in 3 vols.)[3]) and of greater density (d often more than 0.9) than oils distilled with water. As the indications of the United States Pharmacopœia (ninth edition) regarding density ($d_{25^\circ}^{25^\circ}$ 0.875 to 0.888) and solubility (soluble in 3 vols. 70 per cent. alcohol) are exact only for the latter kind of oils, it ought to be revised, as nowadays the majority of lavender oils are distilled by steam.

In connection with the second Lavender Congress, held at Digne on October 1st last year, as mentioned before, Lautier Fils and Roure-Bertrand Fils published a paper each on lavender oil[4]). Lautier Fils tried to decide the question whether the quality of a lavender oil depends on its ester content. For this purpose, three samples of lavender grown in the same district, Saint André de Neouilles, were distilled under identical conditions; viz., 100 kilos of flowers, under a vapour pressure of 7 kilos, for 45 minutes[5]): — a) dry wild lavender, distilled 15 days after collection, b) fresh wild

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[1]) *Perfum. Record* 12 (1921), 404. — [2]) Comp. also our experiments, *Report* April 1907, 64. — [3]) These indications are not generally valid, as we have repeatedly distilled lavender oils by steam in the South of France which dissolved in 3 vols. of 70 per cent. alcohol. — [4]) *Perfum. Record* 12 (1921), 342. — [5]) This indication is of no value, as the pressure sinks at once to that of the outer atmosphere, if the still is in connection with it through rising-tube and condenser.

lavender immediately after collection, c) fresh cultivated lavender immediately after collection. The mean of a large number of analyses of the oils obtained gave the following results: —

Lot.	Density at 15°.	Solubility in 70 per cent. alcohol,	α_D.	Esters as linalyl acetate.
a	0.894	5 vols. with difficulty	5° 45'	56.4 per cent.
b	0.889	3 „	7° 20'	50.8 „ „
c	0.887	3 „	7° 50'	52.1 „ „

The three oils were submitted to distillation with a current of steam under reduced pressure, giving the subjoined results: —

(a) essential oil 79, resinous residue 21 per cent.
(b) „ „ 92, „ „ 8 „ „
(c) „ „ 96, „ „ 4 „ „

The resinous residues hat little odour, but gave the following percentages of ester: — (a) 65.4, (b) 62.3, (c) 62.6.

The authors conclude from these results that the figures representing the total ester content are misleading and that it would be necessary to deduct the ester content of the inodorous resinous residues, when the real percentages of ester would be: — (a) 42.7, (b) 45.8, (c) 49.6[1]).

It further results from the experiments that lavender which has been piled up to await distillation always gives a false titration, as resins with high ester content are formed by oxidation at the expense of the essential oil. According to Lautier Fils, the essential oils drawn from such flowers possess neither body nor fineness, although they are pure and have high titration figures for esters. They say that the value of lavender oil depends upon its "body" and upon its "bouquet", which had nothing to do with the percentage of esters, and that oils from the Alps with only 26 per cent. of esters were often far more valuable on account of their "bouquet", than other products with 45 per cent.[2]).

The authors come to the following conclusions, which do not contain anything new: — Bouquet and body are two distinct factors. The body is approximately indicated by the ester titration. Absence of artificial esters must be ensured, in order that the titration figures should be genuinely indicative of value and purity. — There is no clear answer, however, to the question put in the beginning.

We would say that these investigations do not alter the fact that, generally speaking, the value of lavender oils depends upon the percentage of esters. The more careful and appropriate the distillation of the lavender oil, the higher the percentage of esters and the less damage is done to the bouquet.

The paper from the Roure-Bertrand Fils Laboratories[3]) contains extensive, though not altogether new details regarding the distillation, composition, analysis and adulteration of lavender oils. The best lavender oils are obtained, if due attention is given to the following points: — 1) When distilling by direct heat, the flowers ought not to be soaked in water beforehand. The still must not be filled with too much water, as an excess of water diminishes the yield of oil and impairs its quality. 2) The distillation

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[1]) The authors seem to have overlooked that a second steam distillation must needs cause a further saponification of esters and an alteration of the oil. It is not stated whether the distillation was carried out under ordinary pressure or *in vacuo*. — [2]) This has been pointed out already by Birckenstock. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 428. — [3]) *Perfum. Record* 12 (1921), 344.

should be carried through as quickly as possible (within an hour). 3) In consequence special stills with wide neck and wide steam-pipes must be used. 4) The oil passing over has to be cooled well, as cold water dissolves less oil than warm water.

In order to obtain a uniform good product, growers ought to combine and distil the oil in joint distilling plants.

A report has been published on the meeting of the Lavender Commission, held on May 17th, 1921, in the French Ministry of Commerce, containing the suggestions and propositions made by lavender growers, merchants and industrials. The Commission, however, has not arrived at a definite solution of all the questions concerning lavender[1]).

Lautier Fils[2]) examined a lavender oil of the following constants: — d_{15o} 0.894; a_D — 4° 35'; soluble in 3 vols. of 70 per cent. alcohol; ester v. 48.8. In their opinion it had been adulterated with lauric ester, obtained apparently from the residues of cocoa butter manufacture, and small quantities of terpenyl acetate.

According to Humbert[3]), the sub-species of *Lavandula fragrans* and *L. delphinensis*, created by Jordan, cannot be considered as distinct species, but merely as two extreme forms of variation in accord with the local conditions of habitat. Whereas the xerophilous *Lavandula fragrans* predominates in the sunny South of France and on the dry crests of the low mountains, the more moisture-loving *L. delphinense* thrives in the North, or in the higher valleys and higher mountains, where mists and rain are less rare, or again in the shadow of forests. Thus the Luberon shows on its arid brows (calcareous, of the lower Cretacean system), towards 1000 m. high, the most xerophil forms. But on descending from the summit towards the north, one meets on the slopes, less exposed to the sun and principally towards the base, where the soil is no longer purely calcareous, but a soft Miocene formation and more hygroscopic, the whole gamut of transitions to forms presenting the maximum lengthening of axes and enlargement of the leaves. The transformation of one form to the other can be proved experimentally by planting the seed of the xerophil type in a damper soil or climate than the original station, or *vice versa* with the other type. The plant called *L. Faucheana*[4]) by Briquet and Rouy is also only a form of variation.

It is otherwise with *L. pyrenaica*, DC., which plant, found in the eastern Pyrenees, is distinguished by the much greater size of its principal bracts, which are as broad as long and almost conceal the calyx. The flowers are a little larger and the inflorescence appears bigger than that of *Lavandula officinalis*. The vast colonies of *L. Pyrenaica* begin where spike ceases and almost reach the summit of the mountains.

Very seldom, in altitudes of from 800 to 1500 m., the white variety of lavender occurs. It was found on the Mount Angèle near Nyons, in the neighbourhood of Saturnin-les-Apt, on the Ventoux and near Ribiers. The corolla was white in each case, the calyx either blue, red or white. In order to obtain the essential oil of this highly fragrant species, A. Chiris[5]) tried to cultivate the plant from seeds. But only a few seedlings had white flowers, those of the others being mostly very pale. The oil obtained from the latter surpassed the ordinary lavender oil in ester content and aroma[6]).

It results from Humbert's explantions that the bracts and bracteoles are of special importance for the recognition of the different species and varieties of lavender. J. Gattefossé[7]), in an article on French lavender and its hybrids, publishes six pictures

[1]) *Parfum. moderne* 14 (1921), 153. — [2]) *Perfum. Record* 12 (1921), 343. — [3]) *Perfum. Record* 12 (1921), 252. — [4]) This type is not mentioned in the *Index Kewensis* up to 1910. — [5]) *Perfum. Record* 12 (1921), 405. [6]) There are no further details. — [7]) *Parfum. moderne* 14 (1921), 207.

of such bracts and bracteoles of *Lavandula officinalis*, Chaix, *L. latifolia*, Vill. and *L. pyrenaica*, DC. and their hybrids, taken from the *"Office national des Matières premières végétales"*. According to Humbert, the hybrids of lavender and spike are more widely distributed than it was hitherto believed. Very frequent is the hybrid *"Lavandula latifolia < officinalis"*, in which the properties of *L. officinalis* preponderate, so that the gatherers do not know how to distinguish it from the true kind. The other hybrid, *L. latifolia > officinalis*, so-called "lavandin", resembling more *L. latifolia*, is better known to the distillers and avoided by them. Perhaps the lavender-fields in England and in Pornichet (Loire-Inférieure), which both yield oils of a low ester percentage, are cultivations of the hybrid *"L. latifolia < officinalis"*.

Humbert states further that *Lavandula Burnati*, Briq. of the Maritime Alps and *L. hortensis*, Hy.[6]) resemble the "lavandin", whereas *L. Spica-latifolia*, Albert, of the Var and *L. Burnati* var. *Fouresii*, Coste, of the Causses de l'Aveyron, are more similar to *"A. latifolia < officinalis"*.

As regards two hybrids of *Lavandula latifolia*, Vill. and *L. officinalis*, Chaix, see page 118 of this *Report*.

Oil of Lavandula Stoechas. — As results from the investigations of Roure-Bertrand Fils[1]), the oil of *Lavandula Stoechas*, L.[2]), described by us some years ago and which we afterwards designated as originating from *L. dentata*, L.[3]), came in reality from *L. Stoechas* after all. The confusion was due to the fact that we had originally received (1905) from Spain the flowers of the real *L. Stoechas*, whereas the second time (1915), when we asked again for the same kind, in order to have the plant determined by a botanical authority, the flowers of *L. dentata* were sent us by mistake. The sender maintained, however, that in either case the flowers had been taken from the same plant. — Roure-Bertrand Fils state that the oils obtained by them in different years (1906) and 1921) from French *Lavandula Stoechas* differed verry little from one another and from the oil distilled by us (in 1905 from Spanish material), the constants being: — d_{15^0} 0.945 to 0.948, $\alpha + 47^\circ$ to $+49^\circ 56'$, acid v. 0.69 to 0.93, sap. v. 8.40 to 18.67, ester v. 7.71 to 17.74, ester v. after acetylation 47.14, soluble in 5 vols. and more of 60 per cent. alcohol. The principal constituents of the oil are *d*-camphor (semicarbazone, m. p. 238°), *d*-fenchone (oxime, m. p. 165°). Besides, fenchyl alcohol and perhaps terpineol and a phenol seem to be present.

In order to obtain pure fenchone, the authors oxidized the oil with nitric acid and heated the product of the reaction repeatedly with 10 per cent. aluminium chloride. The resulting fenchone had the following constants; m. p. $+3$ to 5°, d_{20^0} 0.9443, $\alpha_{D20} + 54^\circ 34'$, n_{D21^0} 1,4625, m. p. of the semicarbazone 174 to 176°.

Roure-Bertrand Fils publish simultaneously an illustrated extensive botanical study by A. Camus regarding *Lavandula Stoechas* is, like rosemary, according to its whole structure a xerophilous plant which can stand a good deal of drought. It thrives on arid slopes, exposed to the sun, on heaths and steppes, frequently together with *Cistus* and *Calycotome* species, along the coast of the Mediterranean from Gibraltar to Asia Minor, on the Canaries, in Madeira, Portugal, Spain, Menorca, Sardinia, France, Corsica, Italy, the Balkans, Crete, Syria, Palestine, Morocco, Algeria and Tunis. *Lavandula dentata*, however, does not occur in France, but only in the coastal regions of part of the Mediterranean countries, such as Spain, Morocco, Algeria and perhaps southern Italy.

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[1]) *Bull. Roure-Bertrand Fils*, Oct. 1921, 3. — [2]) Comp. *Reports* October 1905, 10; April 1908, 62. — [3]) *Report* April 1915, 28.

Lemongras Oil. — Two samples of this oil was forwarded to the Imperial Institute from Seychelles. One of these samples was stated to have been obtained from *Andropogon Schoenanthus*, L. = *Cymbopogon citratus*, Stapf, which has been grown in Seychelles for a long period. The oil had the following constants: — $d_{15°}^{15°}$ 0.883, $\alpha_{D20°}$ —0° 12', $n_{D20°}$ 1.486, insoluble in 70 per cent. alcohol, practically soluble in 0.9 vol. 80 per cent. alcohol at 15°, becoming turbid on dilution; citral, determined by the bisulphite method, 78.5 per cent. The oil is therefore of similar character to the West Indian lemongrass oil. The sample was valued in London at about 6 d. per oz., when commercial lemongrass oil. was quoted at 8 d. per oz. (February 1919).

The second sample was stated to have been derived from a variety of lemongrass *(Cymbopogon flexuosus?)* introduced into the colony from Cochin in 1911. The golden-yellow oil showed an odour resembling that of lemongrass and also that of citronella oil. The constants were: — $d_{15°}^{15°}$ 0.898, $\alpha_{D20°}$ —10° 12', $n_{D20°}$ 1.484, insoluble in 70 per cent. alcohol, soluble in 1 vol. 80 per cent. alcohol at 15°, becoming slightly turbid with 3 vols.; citral, 38 per cent. (bisulphite method); geraniol, 20.5 per cent. These data show that the oil differs markedly in composition from the East Indian oil and suggest that this "lemongrass" oil is not derived from *Cymbopogon flexuosus*, but from some other species. Possibly it may ever be a mixture of lemongrass and citronella oils.

We gather from and English periodical[1]) the following statements concerning the so-called West Indian lemongrass oil derived from *Cymbopogon citratus*, Stapf which is known to differ from the East Indian oil by its low solubility in alcohol. The oil was originally distilled in Travancore and came to England via Cochin for the first time in 1832. When later the industry extended northwards to Malabar, Calicut became the centre of distribution. Recently, the oil is being distilled in Assam and Java. Before the war, from 2000 to 3000 cases, each containing one dozen quart bottles of oil (each .1.236 litres) were exported annually from Cochin to Bombay as well as to New York, Hamburg, and London.

Oil of Leptospermum flavescens. — In the oil of *Leptospermum flavescens* var. *citratum*, Challinor, Cheel and Penfold[2]), some years ago, proved the presence of a phenol yielding a benzoate of the m. p. 67°. This phenol, termed *leptospermol*, has now been investigated closely by Penfold[3]). The amount of the phenol in the oil varied according to the different localities from which the material was collected, and ranged between 0.75 and 8.0 per cent. The leptospermol ($C_{14}H_{20}O_4$?) was abstracted from the oil by shaking with a 3 per cent. caustic soda solution and was a somewhat viscous liquid, almost colourless, with a pleasant and characteristic odour, and the following constants: — b. p. 145 to 146° (10 mm.), 275 to 278° (770 mm., uncorr.), $d_{20°}$ 1.073, $\alpha \pm 0$, $n_{D20°}$ 1.5000. In alcoholic solution, it gave with ferric chloride a brilliant distinctive orange-red coloration; with copper salts, an intease blue coloration. Derivatives of the phenol were not obtained. The phenol bears a very strong resemblance to the phenol tasmanol[4]) found in various eucalyptus oils, but differed therefrom by the refractive index and the boiling-point under reduced pressure.

Oil of Leptospermum grandiflorum. — From the leaves of *Leptospermum grandiflorum*, Lodd., a myrtacea growing in the river-beds in New South Wales, A. R. Penfold[5]) obtained 0.61 per cent. of a rather viscous, dark brown oil. After shaking with dilute

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[1]) *Perfum. Record* 12 (1921), 50. — [2]) Comp. *Report* 1919, 34. — [3]) *Perfum. Record* 12 (1921), 336. — [4]) Comp. *Report* 1916, 32. — [5]) *Journ. Proceed. of R. S. of N. S. W.* 54 (1921), 197. Acc. to *Bull. Roure-Bertrand Fils*, October 1921, 159.

sodium hydroxide solution the oil exhibited the following constants:— d_{15° 0.9324, α_D — 2° 42′, n_{D20° 1.5048, ester v. 7.2, ester v. after acet. 40.98; insol. in 10 vols. of 80 per cent. alcohol. By repeated fractionation of the oil in presence of sodium, under 10 mm. pressure, the auther obtained the fractions: — 123 to 125° (d_{15° 0.910, α_D — 6.2°, n_{D20° 1.4967) and 129 to 132° (d_{15° 0.921, α_D + 0.72°, α_{D20° 1.5063). These two fractions, which agreed in their constants fairly with aromadendrene and eudesmene[1]), gave likewise the colour reaction of these sesquiterpenes with bromine and with sulphuric acid[2]). In addition, the oil contained, besides a small amount of phenolic bodies, a sesquiterpenic alcohol, which the author was unable to describe more closely.

Oil of Leptospermum odoratum. — On distilling the leaves and twigs of *Leptospermum odoratum,* Cheel, a plant likewise occuring in the valleys of New South Wales, A. R. Penfold[3]) obtained on the average 0.75 per cent. of a yellow oil with an odour reminding of terpenes and roses. Its constants differed according to the time of collecting (August, 1917, May and October, 1920) and ranged as follows: — d_{15° 0.9163 to 0.9280, α_D — 16,32 to — 33.02°, n_{D20° 1.4960 to 1.4990, ester v. 5.6 to 7.2, ester v. after acet. 57.00 to 91.93, sol. in 10 vols. of 80 per cent. alcohol, in one case insoluble in 80 per cent. alcohol. In addition to combined acetic acid, the oil contained above all butyric acid in combined state. In the fraction b. p. 60 to 90° (10 mm.), α- and β-pinene were proved to be present by means of characteristic derivatives[4]). The fraction 125 to 140° (10 mm.), one-half of the oil, contained nearly equal parts of eudesmene and aromadendrene which were identified by means of their constants and their colour reactions[5]). This natural eudesmene differed from the synthetical dextrorotatory preparation[6]) by its optical rotation of — 53°. From the solid distillation-residue (10 to 15 per cent. of the oil), there was obtained, by crystallisation from dilute alcohol, eudesmol, m. p. 79 to 80°, b. p. 156° (10 mm.), $[\alpha]_{D20^\circ}$ + 31.80°. Furthermore, the oil appeared to contain about 2 per cent. of an alcohol not further dealt with, which gave rise to the rose-like odour of the oil.

Oil of Lindera sericea. — A. Spann[7]) reports that according to official Japanese statistics an essential oil is distilled from the lauracea *Lindera sericea*, Blume (Kuromoji[8])). The producing districts, Hiogo *ken*, Shimane *ken* and Hiroshima *ken*, are in the southern part of the main island Honshiu. In 1915, 9438 kin of oil were obtained, representing a value of 9880 yen.

Machilus Oil. — Seisi Takagi[9]) obtained from the wood shavings of the Formosan Lauracea *Machilus Kusanoi*, Hayata[10]), on distillation, a pale yellow, viscous oil with the constants: — d_{40}^{270} 0.9815, $[\alpha]_{D20^\circ}$ + 18.20°, acid v. 0, sap. v. 0, sap. v. after acet. 50.21. On fractionation under 5 mm. pressure, 120 g. of the oil gave 6 g. oil b. p. 125 to 140°, 42 g. b. p. 140 to 149°, 25 g. b. p. 149 to 159°, 9 g. b. p. 156 to 170° — these three

¹) Cf. *Reports* April 1902, 31; October 1913, 59. — ²) In the literature, colour reactions are only given for aromadendrene (cf. Baker and Smith, *A Research on the Eucalypts*, 2nd ed. p. 417; Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed. vol. III, p. 275) but not for eudesmene. — ³) *Journ. & Proceed. of R. S. of N. S. W.* 54 (1921), 197. Acc. to *Bull. Roure-Bertrand Fils*, October 1921, 159. — ⁴) Details in this respect are missing in the abstract. — ⁵) Cf. the footnote above, with *Lept. grandifl.* — ⁶) Cf. *Report* October 1913, 59. — ⁷) *Der Tropenpflanzer* 24 (1921), 167. — ⁸) Details concerning the Kuromoji oils obtained from the leaves and other parts of the plant are to be found in Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 502. — ⁹) *Journ. pharm. Soc. Japan* 1921, No 473 (2nd communication). From a copy kindly forwarded to us. Unfortunately, we hitherto did not come across either the first communication or an abstract thereof. — ¹⁰) Is not mentioned in the *Index Kewensis* of 1910.

fractions solidify to a crystalline mass —, and 10 g. of a viscous oil, b. p. 170 to 185°. Repeated crystallisation of the solid fractions yielded a body $C_{15}H_{26}O$, *machilol;* m. p. 79 to 80°, b. p. 160° (14 mm.), $[\alpha]_{D25°} + 42.87°$. On treatment with acetic anhydride and sodium acetate the body is acetylated but partly; neither is formed a phenylurethane with phenyl*iso*cyonate nor a benzoate according to Schotten-Baumann. Reduction with platinum black and hydrogen yielded dihydromachilol $C_{15}H_{28}O$, m. p. 82 to 83°, b. p. 157 to 158 (14 mm.), $[\alpha]_{D18°} + 16.43°$. By oxidation with potassium permanganate, machilol passed over into dihydroxymachilol, or machilene glycerol $C_{15}H_{28}O(OH_2 + H_2O$, m. p. 110°, $[\alpha]_{D18°} - 25.91°$; monobenzoate, m. p. 142°. This body proved to be identical with α-dihydroxyatractylol which the auther obtained, in addition to β-dihydroxyatractylol (m. p. about 78°, $[\alpha]_{D18°} + 24.68°$), on oxidising atractylol by the same reagent. Hence, machilol is a bicyclic, tertiary sesquiterpene alcohol.

When machilol was heated with formic acid, machilene $C_{15}H_{24}$ resulted; b. p. 120° (3 mm.), $d_{40}^{23°} 0.9109$, $[\alpha]_{D20°} + 58.73°$, $n_{D20°} 1.51257$; Liebermann's reaction: first blue, then green, and after some standing dark blue. On reducing machilene with hydrogen and platinum in glacial acetic acid, tetrahydromachilene $C_{15}H_{28}$ was formed; b. p. 132° (11 mm.), $d_{40}^{19°} 0.8964$, $[\alpha]_{D19°} + 37.04°$, $n_{D19°} 1.48645$.

Machilene is no uniform body, but a mixture of probably two isomerides, for on abstracting water from machilol by weaker-acting reagents, an isomeride of machilene is formed with higher rotatory power (α_D about $+ 100°$).

On reducing atractylene (b. p. 108 to 109° [3 mm.], $d_{40}^{18°} 0.9189$, $[\alpha]_{D18°} + 78.35°$, $n_{D18°} 1.51795$) catalytically, tetrahydroatractylene is formed (b. p. 129 to 130° [10 mm.], $d_{40}^{11°} 0.9030$, $[\alpha]_{D12°} + 36.99°$, $n_{D12°} 1.49589$), a liquid with a feeble but pleasant odour.

Since the tetrahydro derivatives of machilol and atractylol agree very closely in their qualities, Takagi ascribes to atractylol (or atractylene) and to machilol (or machilene) the same carbon nucleus, both bodies differing merely by the position of the double linking and the hydroxyl group.

Massoi Bark Oil. — According to the Imperial Institute[1]), the Massoi bark from the Fiji Islands and New Guinea and sold on the Singapore market, comes from *Cinnamomum pedatinervium,* Meissn. (identical with *Massoia aromatica,* Beccari [?])[2]).

Milfoil Oil. — An extensive publication on this oil has been published by R. E. Kremers[3]). The crude material, *Achillea Millefolium,* L. serving for the investigation was collected from the middle of June to the middle of July, freed carefully from foreign matter, and dried immediately at the open air. About 1200 pounds of fresh herb weighed after three days' drying 420½ pounds or 190.7 kilos, and yielded 892 g. of oil, or 0.467 per cent. of the dry herb. This exceptionally high[4]) yield of essential oil was arrived at by cohobating the distillation-water, thus obtaining in addition to the principal oil, 21 per cent. of "water oil", calculated on the former oil.

Firstly, the "water oil" was subjected to fractional distillation. The fractions, b. p. between 64 and 90°, proved to contain formaldehyde (by its odour, and Schiff's reagent), methyl alcohol (methyl salicylate, formaldehyde, and *3,5*-dinitrobenzoic methyl ester), ethyl alcohol (iodoform reaction), acetone (reaction with sodium nitroprusside and iodine potassium iodide), furfural (aniline acetate), borneol (m. p. 203 to 204°).

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[1]) *Bull. Imp. Inst.* 19 (1921), 338. — [2]) As to the still doubtful origin of the Massoi bark of commerce see Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 498. — [3]) *Journ. Americ. pharm. Assoc.* 10 (1921), 352. — [4]) From dried blossoms once even 0.485 per cent. oil were obtained, from fresh blossoms, as a rule, 0.07 to 0.25 per cent. Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 617.

The constants of the principal and the aqueous oil (together with those observed by Miller[1]) in 1916 were as follows: —

	Principal oil		Aqueous oil	
	1916	1919	1916	1919
d_{170}	0.915	0.913	d_{250} 0.939	0.948 and 0.959
Acid value	7.24	4.27[2])	37.0	—
Ester value . . .	2.2	5.65[3])	7.6	17.7
Sapon. value . .	9.44	10.92[2])	44.6	—
Ester v. after acet.	23.5	17.8	51.8	50.9

These figures show that the water oils contain more free acid, more esters and more free alcohols than the principal oils. The following constituents of the cohobated oil were identified: — A valeric acid (in all probability; silver salt), a large quantity of impure borneol, furfural (aniline acetate reaction), and traces of eugenol (benzoate, m. p. 69 to 70°).

The main oil was separated by fractionation, first under atmospheric pressure, into 10 fractions boiling between 85 and 174°, then under 30 mm. pressure, into 10 more fractions boiling between 75 and 125°. Miller[3]) had proved formerly the presence in these fractions of following bodies: — valeric, salicylic and butyric acids, aldehydes, pinene, limonene, camphor, borneol, and cineole. In addition to these constituents which, except limonene, were also identified by Kremers, the latter author succeeded in identifying nopinene (nopinic acid, m. p. 126°; nopinone semicarbazone, m. p. 188°). The constants of a saponified fraction of the b. p. 90 to 95° pointed to the presence of thujone (d_{250} 0.929, α — 3.0°, n_{D250} 1.4588). The tribromide (Wallach) showed the m. p. 121°; the semicarbazone was readily formed, but was either a mixture of the derivatives of α- and β-thujone, or of thujone with that of another ketone.

From 100 g. of a fraction boiling above 140°, Kremers obtained 35.5 g. of a blue oil, containing azulene, b. p. 135 to 136° (1.1 mm.), and 59 g. non-blue oil. With alcoholic picric acid solution, azulene yielded instantly the picric acid addition compound. After removal of the azulene by means of phosphoric acid, the oil was fractionated (pressure, 5 to 0.1 mm.) into 8 fractions boiling between 80 and 180°. From the portions boiling between 100 and 115° (0.5 mm.) the author obtained, by distillation with sodium, a fraction with the constants: — b. p. 105 to 110°, d_{200} 0.916, α — 13.75° (100 mm. tube), n 1.4990, mol. refr. 65.4, which yielded a benzylamine base, m. p. 172 to 173°, and a hydrate, m. p. 94 to 95°. The presence of caryophyllene, therefore, must be considered as proved.

As a supplement to Kremers' notes on the work of Miller on milfoil oil, we add the following statements culled from Miller's paper, the copy of which reached us only recently. E. R. Miller[3]) obtained by steam-distillation partly from the entire (fresh or dried) plant, partly from the flowers or the leaves of Achillea millefolium, L. cultivated near Madison a series of oils, all of which were dark blue. The flowers yielded more blue oil than the leaves. Distillation of the lower two-thirds of the plant is unprofitable. Drying of the plant apparently produces no change in either the quantity or quality of the oil. Apparently, there exist some definite relations between yield on one hand and density and refractive index on the other. As stated above, Miller separated the oil into various fractions and proved the existance of following constituents in the oil: — l- and d-pinene (nitrosochloride, m. p. 102 to 103°; nitrolpiperidin, m. p. 119°), l-limonene (?)

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[1]) Cf. *Bull.* 785, *University of Wisconsin.* See also further below on this page. — [2]) These figures do not agree with each other. — [3]) *Bull. Univ. Wisconsin* No. 785.

(odour and density of corresponding fractions, no nitrosochloride being obtained), *l*-borneol (m. p. 202 to 203°; acetate, m. p. 29°; phenylurethane, m. p. 139°), bornyl acetate and other borneol esters, *l*-camphor (oxime, m. p. 119°; semicarbazone, m. p. 235 to 236°), cineole (resorcinol compound; iodole derivative, m. p. 106 to 107° instead of 111 to 112°), salicylic acid (colour reaction with ferric chloride), aldehydes (presumably two, Schiff's reagent), formic, acetic, butyric (?), and *iso*valeric acids (silver salts), a non-volatile acid or a lactone, and a blue constituent of high b. p. (145° at 15 mm.).

Monarda Oils. — A series of methoxyl estimations in monarda oils undertaken partly with unchanged oils, partly after removal of the phenols in the hope that this constant would prove characteristic, has been published by D. C. L. Sherk[1]. In the oils of *Monarda punctata*, the content of methoxyl amounted to 0.11 to 0.36 per cent. The non-phenolic parts of the oils differed in their methoxyl value hardly from the original oil. Hence, on the separating of the phenols a methoxylated body must have dissolved in the aqueous alkali. Such a body is the monomethyl ether of thymohydroquinone, since the dimethyl ether and thymol methyl ether, otherwise constituents of the oil, are non-phenolic bodies, *i. e.*, insoluble in alkali. Sherk was able to prove that the alkaline extract of an oil from *Monarda fistulosa* contained a pale reddish oil with 1.14 per cent. methoxyl and leaving on distillation a tarry residue with 0,95 to 1,17 per cent. methoxyl. The part of the oil extracted from the alkaline liquid by means of ether contained, in addition to carvacrol, thymohydroquinone.

From an oil of *Monarda punctata*, the thymol of which had been removed for the greater part by freezing, Sherk obtained crystals of thymohydroquinone and a black, tarry residue with 0.61 to 1.48 per cent. methoxyl. This residue consisted for one-third of thymohydroquinone, m. p. 141°, which was isolated therefrom by fractional distillation.

It is well-known that the essential oils obtained by redistillating the distillation-water of essential oils show properties differing from those of the principal oil. In the most cases, especially the specific gravity of the latter oil is lower than with the "water oil", as the water-soluble constituents of essential oils show, as a rule, a higher density than the bodies insoluble in water. As we gather from a paper by E. R. Miller[2] on "Redistillation of aqueous distillates resulting from the production of volatile oils", the specific gravity of the principal oil from *Monarda fistulosa*, L. amounted to 0.9280, with the "water oil" of the same plant, to 0.9700. Wormwood oil, however, behaved according to Miller, differently, since the "water oil" was lighter owing to the content of thujone. The yield of wormwood "water oil" ranged between 6 and (?) 37 per cent. of the aqueous distillate, according to the maturity of the plants under investigation.

Oil of Mosla grosserata. — Y. Murayama[3] discovered in the oil of *Mosla grosserata*, Maxim., a new terpene, moslene (comp. p. 50 of this *Report*).
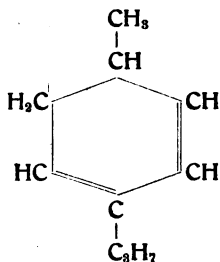
Oil of Mosla Hadai. — As we hear from Asahina, the oil[4] investigated some years ago by Y. Murayama did not come from *Mosla japonica*, Maxim., but from *Mosla Hadai* Nakai[5]. (Comp. also lower down.)

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[1] Fritzsche Bros. Fellow, 1919/20. *Journ. Americ. pharm. Assoc.* 10 (1921), 417. — [2] *Midland Druggist and pharm. Review* 54 (1920), 146. — [3] *Journ. pharm. Soc. Japan* 1921, No. 475. — [4] Comp. *Report* April 1910, 78. — [5] The *Index Kewensis* does not mention it up to 1910.

Oil of Mosla japonica. — Since Hada's discovery of thymol in the oil of *Mosla japonica*, Maxim. this plant has been cultivated in Japan with the object of obtaining this phenol. On investigating the terpene fractions of the oil[1], Y. Murayama[2] found a new terpene named by him *moslene*. This body was found in a fraction with the b. p. 59 to 60° (10 mm.) or 173 to 175° (ord. pressure) obtained from an oil after the thymol had been removed with alkali. The fraction, which was not quite free from oxygen, showed some resemblance with the terpene crithmene obtained by Francesconi and Sernagiotto[3] from Italian samphire oil, and had the following constants: — d_{18^0} 0.8528, n_D 1.48228; nitrosochloride m. p. 111°, nitrolpiperidide m. p. 142 to 143°, nitrolanilide m. p. 126 to 128°, dihydrochloride m. p. 52°, nitrosate m. p. 114°.

On treatment of the nitrosochloride, in alcoholic solution, with sodium, a body $(C_{10}H_{13})_2N_2O$ resulted; yellow needles, m. p. 52 to 53°; sometimes, a less soluble substance $(C_{10}H_{13})_2N_2$, orange-yellow leaflets, m. p. 85 to 87°, was formed, which proved to be identical with azo-*p*-cymene (m. p. 87°); formation of the latter by reduction of *p*-nitrocymene. The identity of the yellow body (m. p. 52 to 53°), too, with azoxy-*p*-cymene, is, in Murayama's opinion, established, in so far as the yellow body and azoxy-*p*-cymene, on reduction, both give rise to the identical benzidine derivatives $([C_{10}H_{13}\cdot NH_2\cdot HCl]_2,$ decompos. p. 292°).

I. 1 : 2-Dihydrocymene.   II. 1 : 4-Dihydrocymene.

According to Murayama, moslene, therefore, is a dihydrocymene, with two double bonds located most probably in the benzene nucleus. Since amongst the five isomerides complying to these conditions three are known, *i. e.*, α-terpinene, γ-terpinene, and α-phellandrene, moslene appears to be constituted as stated in one of the above formulæ.
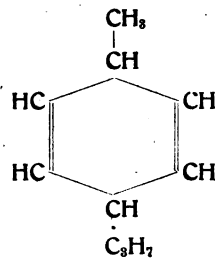
Mustardseed Oil. — Up to now it was only known that the insoluble deposits, forming sometimes in mustardseed oil, consisted of an orange yellow compound, containing carbon, nitrogen, hydrogen and sulphur. H. Kunz-Krause[4] investigated this compound more closely. He comes to the conclusion that it is not a uniform body, but is composed of allylamine sulphate, soluble in water, and *pseudo*-sulphocyanogen, insoluble in water. In addition to these two chief compounds, there are present most likely small quantities of xanthogenic acid derivatives, *iso*-sulphocyanic acid and allyl-substituted urea. As the constituent of the deposit which could be washed out with water, smelled distinctly of mustardseed oil, after having been stored over caustic lime for several months, the author thinks that the insoluble part decomposes and splits off allyl mustard oil. It is probable that a solid polymeride of *iso*-sulphoallyl cyanide $(S = C = N - C_3H_5)_n$ forms, perhaps in combination with *pseudo*-sulphocyanogen, $C_3HS_3N_3$, formerly called per-sulpho-cyanogen[5]). The author gives as the reason for the formation of the deposit and of the other accessory compounds always present in mustardseed oil, the decomposition of three molecules of mustardseed oil in sulphur and allyl cyanide, and certain intramolecular changes of the mustardseed oil, due to

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[1] Cf. *Bericht* (German) 1920, 42. — [2] *Journ. pharm. Soc. Japan* 1921, No. 475. According to a reprint kindly forwarded to us. — [3] Cf. *Report* October 1913, 94. — [4] *Arch. der Pharm.* 259 (1921), 16. As per a reprint kindly sent us. — [5] I. Maier, *Die ätherischen Öle*, Stuttgart 1862, p. 167.

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the influence of air, light and moisture. In consequence, mustardseed oil ought to be kept always in small, absolutely dry vessels and guarded against air and light.

According to A. Cauda[1]), the percentage of mustardseed oil is smaller in southern districts (Sicily), than in the more northern regions (Piemonte, Forli), the content of oil being the smaller, the greater the content of fatty oil. During germination, the content of mustardseed oil, which diminishes on etiolation, remains fairly constant. Black mustardseed contained 0.284 per cent., the green germs 0.280 per cent., the etiolated germs 0.170 per cent. of essential oil, calculated with reference to air-dried substance. The test was carried out by oxidizing mustardseed oil with bromine water and depositing the sulphuric acid formed as baryum sulphate.

V. Massera[2]) states that the Italian Pharmacopœia, 3rd edition, contains erroneous indications for the determination of mustardseed oil. Instead of 9.5 to 10 cc. of ammonium sulpho-cyanide solution, 15 to 15.5 cc. are required[3]).

Neroli Oil.—See Orange Blossom Oil, p. 53 of this *Report*.

Oil of Ocimum gratissimum.— An oil of this plant originating from Mahé (Seychelles) and differing entirely in character from the oil produced in the Ivory Coast and Central Africa, has been mentioned by us in our *Report* 1919, p. 36, where we quoted the constants. In the meantime, the plant has been identified at Kew as *Ocimum gratissimum*, L., and a sample of the oil ($d_{15^\circ}^{15^\circ}$ 0.996; α_D —12.7°; n_{D20° 1.532; phenols, 55 per cent.) was investigated by O. D. Roberts[4]).

After removing the free acids (0.2 per cent., probably acetic acid) and the free phenols (entirely eugenol, b. p. 252 to 253°; benzoyleugenol, m. p. 69 to 70°), an oil remained resembling in odour the oil of sweet basil, with the constants:— $d_{15^\circ}^{15^\circ}$ 0.9013; α_D —15.0°, n_{D20° 1.513, ester v., 4.5; ester v. after acet. 101.5. On distillation under 20 mm. pressure the oil yielded the fractions:— 1. B. p. 70 to 85° (16 per cent. of the original oil); 2. b. p. 85 to 100° (15 per cent.); 3. b. p. 100—135° (9 per cent.). Fraction 1 consisted chiefly of ocimene (b. p. 70 to 75° [20 mm.]; $d_{15^\circ}^{15^\circ}$ 0.8029; inactive, n_{D20° 1.4855; dihydromyrcene, $d_{15^\circ}^{15^\circ}$ 0.7777; n_{D17° 1.4500; mol. refr. 47.7; tetrabromide, m. p. 88°). Fraction 2 recalled the odour of linalool; on oxidation with chromic acid mixture a citral-like odour was produced. Fraction 3 had a distinct odour of methylchavicol, but judging from the specific gravity, no large proportion of this compound was present.

The composition of the sample, therefore, is approximately as follows:— Terpenes (ocimene), 16 per cent.; phenols (eugenol), 55 per cent.; phenol ethers, calculated as methylchavicol, 5.6 per cent.; alcohols, probably linalool, 13 per cent.; esters, 0.6 per cent.; residue and loss, 9.8 per cent. The oil appears to be rather similar in composition to an oil of sweet basil of the variety *Selasih Mekah* from Java, as examined by van Romburgh[5]).

Oil of Ocimum viride.— A sample of the oil from *Ocimum viride*, Willd. was forwarded to the Imperial Institute from Seychelles in 1919 and revealed on examination[6]) the following properties:— $d_{15^\circ}^{15^\circ}$ 0.910; α_D +0.75°; n_{D20° 1.497; phenols, consisting almost entirely of thymol, 37 per cent., whereas previous samples of the oil of identical origin,

[1]) *Staz. Sperim. Agrar. Ital.* 52 (1919), 544. According to *Chem. Zentralbl.* 1921, I. 814. — [2]) *Boll. Chim. Farm.* 60 (1921), 62. As per the *Chem. Zentralbl.* 1921, IV. 391. — [3]) Years ago, when discussing the Italian Pharmacopœia, we have already pointed out this mistake. Comp. *Report* April 1910, 131. — [4]) *Journ. Soc. chem. Ind.* 40 (1921), T. 164. — [5]) Comp. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 578. — [6]) *Bull. Imp. Inst.* 18 (1921), 348.

investigated in 1917, contanied 52 to 62 per cent.[1]). Equally, the yield of oil in the present instance was less (0.2 per cent.) as compared with the former yields (0.5 and 0.45 per cent.) obtained in 1916 and 1917. It was of importance to as certain whether this low yield of oil was due to faulty distillation or whether it was due to the stage of growth or condition of the leaves. Since the oil is of importance for the manufacture of thymol, it was suggested that the conditions be determined for obtaining the largest yield of oil containing a maximum of thymol.

Olibahum Oil. — See Frankincense Oil, p. 36 of this *Report.*

Orange Blossom Oil. — According to news from the South of France, the probable result of the coming flower crop will be about one fourth of the normal average. As it is known, the trees had suffered from the severe frost in the winter 1919/20 to such an extent that part of them had to be cut down to the roots, whereas from others the largest branches had to be sawn off. These trees, of course, do not come into consideration at all for the next crop. Those, however, which in warmer places were less exposed to the frost have plenty of buds and promise fair, unless there be frosts again before the beginning of May. Nothing can be said so far as to the price of the blossoms, but after having paid 10 francs per kilo in 1920 and Fr. 12.50 in 1921, one hopes to see them this year reduced to about one-half.

W. Niemz[2]) states that the production of neroly oils in Italy, especially in Sicily, which so far had been unable to compete with the French distillates, is improving also in quality. He says that it is scarcely possible to tell any difference between Italian and French oils.

On account of our own experience we are a little more sceptical. What we have seen so far of Italian oils does not come up by far to the French qualities. This holds good even for the samples received quite recently. Apart from the odour, there is a difference in the constants. We have often had the impression that one is a little careless in the selection of the material, distilling not only flowers, but leaves, branches and unripe fruits. It is also possible that the blossoms of the bitter and the sweet orange-trees are used indiscriminately and that the state of development of the blossoms is not sufficiently taken into consideration. In France, only the fully developed blossoms of the bitter orange-tree, gathered with care, are distilled, and this accounts perhaps for the superiority of the French product.

Origanum Oil. — In our *Report* of 1918, page 37, we quoted as a communication of the Imperial Institute[3]) the phrase: "Ordinary Cyprus oil is said to contain merely thymol" and added that this seemed to us rather doubtful. It has been found out meanwhile that the mistake was on our side, as the original English text states correctly: "Cyprus origanum oil only contains carvacrol".

Oil of Orixa japonica. — By steam distillation of the leaves and twigs of *Orixa japonica*, Thunb. *(Celastrus Orixa)*, a celastracea known in Japan as *Kokusagi*, Y. Shinosaki[4]) obtained about 0.01 per cent. of a light brown oil having a characteristic odour recalling that of the oil of *Lindera sericea*, Blume[5]). The constants were: —

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[1]) Comp. *Report* 1918, 36. — [2]) *Deutsche Parf.-Ztg.* 7 (1921), 161. — [3]) *Bull. Imp. Inst.* 15 (1917), 306. — [4]) *Journ. chem. Ind., Japan* 24 (1921), 563. *Journ. Soc. chem. Ind.* 40 (1921), A. 560. — [5]) Hitherto, nothing is known as to the essential oil of this lauracea.

d_{150} 0.8974; $[\alpha]_D$ — 4.5°; n_{D200} 1.4750; soluble in 2 vols. 80 per cent. alcohol; acid v. 0; sap. v. 37.27; sap. v. after acet. 100.3. Its principal constituents are camphene, linalool, a terpene alcohol and its ester[1]).

Orris-root Oil. — The last crop of Florentine orris-root is estimated by competent people at from 250000 to 300000 kilos, a very unfavourable result. The high costs of labour do not induce anybody to having the roots dug up, the less so as there are considerable stocks from last year, owing to the sluggish demand. As these old stocks are said to amount to about 300000 kilos, there would be 300000 to 350000 (?) kilos available, altogether *i. e.* about the same quantity as has been obtained in an average crop of the last ten years. As there is very little business, the dealers try to make the consumers believe that there will be a rise, but it seems rather doubtful whether they will succeed in the long run.

Our two qualities of orris-root oil are in good demand, which proves that they have maintained their leading position in perfumery, in spite of the manifold impediments of the post-war times.

Whereas in Italy, and especially in the province of Florence, *Iris germanica,* L. and *Iris pallida,* Lam., are cultivated above all, in France *Iris florentina,* L. = *Iris alba* is grown almost exclusively, though on a smaller scale. Some few iris plantations are said to be found in the departments of Var and Bouches-du-Rhône, according to A. Roulet[2]). The largest plantation exists in the department of Ain, where the plant was cultivated already in 1835. It covers from 10 to 30 hectares, according to the year. Pellissier[3]) says that the cultivation is restricted to the small communities of Anglefort and Corbonod, comprising a distance of 10 to 15 kilometres on the right bank of the Rhône. The iris, which adapts itself to every calcareous soil, if not too fresh and too. moist, thrives best on good alluvial soil. In Ain the plant is cultivated on tilled, calcareous steppe-land. Very rich soil does not suit the iris, nor should stable manure be given, as it influences the aroma of the rhizomes unfavourably. Artificial nitrogenous fertilizers do not seem to have any effect on the development of the plant, whereas potash compounds favour the aroma and the growth of the rhizomes. Others recommend on the contrary 15000 to 20000 kilos of stable manure or 8 to 10000 kilos of oil cake per hectare after the second or third rotation of crops.

Planting takes place already towards the end of August, for which purpose the young shoots of two-year-old rhizomes are kept. They have no swelling yet, but roots, and are planted 25 to 30 cm. apart in every direction and 10 cm. deep. Sometimes they are first kept in a nursery and planted out in the following autumn.

The best remedy against "iris rot"[3]), it is said, is to improve the soil, in case it should be too damp, and to disinfect it with carbon sulphide (200 grams per square metre).

In the department of Ain, the rhizomes are collected already in the second year, from August to October; in Tuscany, in spring of the third year. The rhizomes are not, as in Italy, first soaked in water, but cleaned and freed from the black skin by women and children. Sometimes the rhizomes are cut in pieces, 5 to 10 cm. long and 3 cm. thick. After having been soaked in water for 24 hours, they are spread on bast mats and dried in the sun or in a moderately warm stove. The yield of a two year old plantation comes up to from 5 to 6000 kilos of dry rhizomes on an average, corresponding to from 10 to 12000 kilos of fresh rhizomes.

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[1]) Details are not given in the abstract. — [2]) *Parfum. moderne* 18 (1920), 154. — [3]) Cf. *Report* October 1915, 65.

Palmarosa Oil. — A sample of this oil, forwarded in 1917 from the United Pro-vinces of India, was investigated in the Imperial Institute[1]) with the following result: — $d^{15^o}_{15^o}$ 0.889; α_D —0.41^o; n_{D20^o} 1.477; sol. in 1.8 vol. of 70 per cent. alcohol; acid v. 1.6; ester v. 11.8; total alcohols, calculated as geraniol, 90.7 per cent. The oil answered nearly fully the requirements of a good commercial quality, yet it smelled slightly of lemons and had not the clean geraniol odour of highest grade palmarosa oil; possibly, the sample contained lemongrass oil.

A second sample of palmarosa oil distilled at Cawnpore contained a lower per-centage of total alcohols and its aroma was not quite equal to that of the previous sample. Its cônstants were: — $d^{15^o}_{15^o}$ 0.889; α_{D20^o} +0.32^o; n_{D20^o} 1.472; sol. in 1.9 vol. 70 per cent. alcohol; acid v. 0.8; ester v. 28.0; total alcohols, calculated as geraniol, 85.5 per cent.

Patchouly Oil. — Whereas the true patchouly plant of commerce, *Pogostemon Patchouli*, Pell., or *P. Cablin*, Benth., is cultivated only to a very small extent in Java, there are extensive patchouly fields in the North of Sumatra, especially near Tapa Tuan in the Atjeh district[2]). In the beginning the natives cultivated the plant, *nilam*, in order to prepare with the aid of its leaves a hair oil for their own use, and the export of the dried leaves did not begin earlier than about ten years ago. The plantations extended in the same proportion as the prices rose (at present 15 florins per picul, as compared with only 3 florins ten years back). Now they are not only restricted any more to Tapa Tuan, but are also found in the districts of Sama Dua, South-Dho, Phoa and Menke.

Before the war, France and Germany were the chief European importers of patchouly leaves. In 1913, France imported 3659 piculs and Germany 4975 piculs from Penang; in 1914, France imported 93 piculs from Singapore and 1655 piculs from Penang, whereas Germany took 2973 piculs from Penang. In addition, considerable quantities went to British India, Hongkong and, since 1911, to the United States. Japan and Canada were buyers for the first time in 1918, the former importing 259 piculs and the latter 481 piculs from Singapore.

According to a report of the Dutch Chamber of Commerce in New York[3]) the distillation of the oil has been started in Atjeh, the export centre of patchouly leaves.

Roure-Bertrand Fils[4]) examined two patchouly oils from the neighbourhood of Kotta-Radja (Sumatra), obtained by distillation of leaves and stems, and found the following constants: —

	leaf oil	stem oil
d_{15^o}	0.9698	0.9739
α	—52° 4'	—54° 8'
acid v.	1.2	8.7
ester v.	6.7	1.3
„ „ after acetylation . . .	26.13[5])	—
solubility in 85 per cent. alcohol	turbid	turbid
„ „ 90 „ „ „	up to 1 vol., turbid in 3 to 4 vols.	in any proportion

[1]) *Bull. Imp. Inst.* 18 (1921), 342. — [2]) *Chem. and Druggist* 96 (1922), 56. — [3]) *Holland and her Colonies* 1 (1921), No. 7, p. 15. — [4]) *Bull. Roure-Bertrand Fils*, April 1921, 18. — [5]) In this case the acetylation is of very little importance, as patchouly alcohol cannot be acetylated quantitatively.

Both samples had a very fine odour, thus distinguishing themselves from the Penang (Singapore) oils. The high specific gravity seems to indicate that the plant, from which they originate, belongs to the Singapore variety[1]).

Two patchouly oils of 1917 and 1919 from the United Provinces of British India, examined by the Imperial Institute[2]), had the following properties: — $d_{15°}^{15°}$ 0.992 and 0.998, $\alpha_{D20°}$? and — 77°, $n_{D20°}$ 1.513 and 1.515, soluble in 0.3 vol. of 90 per cent. alcohol at 15°, acid v. 3.3 and 1.0, ester v. 4.4 and 5.3. It results from these figures that the oils have nothing in common with the Java oil and very little with that from Singapore, whereas they come very close to the distillates obtained in Europe from Singapore leaves.

Peach Oil. — Although many preparations designated as "Peach Oil" or "Peach Essence" have long been in use for flavouring purposes, it is well known that they consist for the most part of purely empirical mixtures of esters and essential oils with other aromatic substances which occur but little or not at all in the fruit whose flavour they are supposed to represent. This has been proved by F. B. Power and V. K. Chesnut[3]) in their recent investigation of the odorous constituents of peaches. The authors used for their experiments the fresh pulp of selected ripe fruits (Georgia Belle), carefully deprived of the pits. This material was subjected to distillation in various quantities (106.6, 108.4, 120.2 and 14.18 kos.), but each time in one operation and without any added water, in a current of steam. The amount of distillate collected was about 65 liters in the three first cases and 12 liters in the last test. This liquid was repeatedly cohobated until the odorous substances were concentrated in volumes of 4.2, 2, 2 and 0.5 liters, respectively. From one such concentrated distillate the authors obtained by repeated extraction with ether 0.00074 per cent. of essential oil. In another case, when 155.6 kilos of peaches were distilled and the whole distillate extracted with ether, the yield of essential oil was 1.2774 grams = 0.00082 per cent. The oil obtained was limpid, pale yellow and possessed an exceedingly fragrant, intense peach-like odour. When cooled somewhat below the ordinary temperature, it formed a concrete transparent mass, which was interspersed with small acicular crystals, the latter evidently consisting of a paraffin hydrocarbon, melting at 52°. The essential oil from peaches is very unstable. When exposed to the air, it becomes converted into a black, viscid mass and loses completely its original fragrance. Only when kept in a hermetically sealed glass tube, it appeared to remain unchanged. The oil probably consisted in the main of the linalyl esters of formic, acetic, valeric and caprylic acids, together with a little acetaldehyde and furfural, the latter having doubtless been produced during the process of distillation by the action of the organic acids on the sugar contained in the fruit. The presence of cadinene, or a compound giving a similar colour reaction (red colouring with glacial acetic and concentrated sulphuric acids), was also indicated.

In order to prove the presence of linalool, the authors saponified 2 litres of the concentrated distillate with 25 grams of pure sodium hydroxide and distilled the saponified liquid, collecting about 800 cc. of the distillate. By extraction of this liquid, which smelled of linalool, with ether, 0.2620 grams = 0.00024 per cent. of a yellowish, oily residue were obtained, containing a small amount of solid substance, probably a hydrocarbon. Oxidation of the oily residue (linalool) lead in the end to a yellowish

[1]) Comp. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 571. — [2]) *Bull. Imp. Inst.* 18 (1920), 346. — [3]) *Journ. Americ. chem. Soc.* 43 (1921), 1725.

oil, which had the pronounced odour of citral. On the addition of Schiff's reagent, it soon developed a purplish colour and it rapidly reduced an ammoniacal solution of silver oxide. A further identification of the citral and, consequently, the linalool, was not possible, the available quantities being too small.

The authors proved further that the saponified distillate, extracted with ether, contained very small quantities of methyl alcohol (oxidation with potassium permanganate led to formaldehyde). The acids were characterized by their silver salts; the aldehydes (acetaldehyde and an aldehyde of higher molecular weight) were prepared from the bisulphite compounds.

In a similar way as in their investigation of the odorous constituents of apples[1]), the authors proved that the aromatic substances of peaches contain traces of acetaldehyde, even if prepared without the assistance of heat.

No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. It may therefore be concluded that amygdalin is restricted to the kernels of the fruit.

Peppermint Oil, American. — Although the use of American peppermint oil is almost out of the question now in Germany, owing to tremendous rate of exchange for the dollar, we were nevertheless able to purchase small quantities of our well-known brand "F. S. & Co.", as abroad; especially in the neutral countries, there are a good many customers for it, who only reluctantly would use another quality instead. Under the influence of the large stocks from 1920 and the general depression in the United States, last year's price of $ 5.75 per pound of good crude oil was no longer to be maintained. The market gave way quickly, especially after the 1921 crop had shown the splendid result of 350 000 lbs., so that it was possible in the end to buy at $ 1.50. This figure attracts the attention of the speculators and it is the talk already now that producers and dealers, who already last winter tried everything in order to prevent the article from declining any further, will not allow the control of the stocks to pass out of their hands. The quantities available were rather important towards the end of 1921 and as the 1922 crop will very probably also give a good result, one may reckon with a continuance of the present low prices, at least for the near future. Besides, a considerable enlargement of the peppermint fields in the West is to be expected, as other agricultural products promise still less benefit for the time being. The absence of the regular German demand makes itself keenly felt, of course, but as long as France and England do everything in order to damage our political economy and to reduce the buying power of our money, it is not to be thought of a recurrence of the former export of American peppermint oil to Germany.

The fiftieth anniversary of the day of their firm's foundation (August 28th, 1871) has induced our New York friends, Messrs Fritzsche Brothers, Inc., to ask their representative in the peppermint districts for an extensive historical report covering the period of 50 years. It contains a good many important data concerning the development of the peppermint oil industry in the United States and we copy some of the details which might interest our readers.

The cultivation of peppermint in the West started as far back as 1852 to 1854, in the County of St. Joseph in Michigan. The distillation took place especially in the towns of Florence, Sherman, and Lockport. In the years from 1858 to 1860, there were about 10 farmers who grew peppermint, each about 30 to 50 acres of hilly land. The

[1]) Comp. *Bericht* (German) 1921, 7.

yield was then from 25 to 30 lbs. of oil in the first, 18 to 20 in the second and 12 to 15 in the third year. The prices ranged in 1852 to 1854 between $ 2.50 and $ 3.50 per lb., the total production being perhaps about 25000 lbs. per year. The system of distillation differed little from the present one, only that then the stills were smaller. Up to 1860 the chief district for peppermint was Wayne County in the State of New York, but later on the importance of the Michigan peppermint fields grew rapidly. Towards the end of the seventies, one started there the cultivation in lower, well-watered districts (marshes) which were easier to work and keep free from weeds. Little by little, the Michigan growers acquired a monopoly, as their costs of production were lower than those of their colleagues in the State of New York. English peppermint plants were first introduced in 1892 and cultivated in thee neighbourhood of Nottaway in the County of St. Joseph. This proved to be a complete success, as the English plants are more hardy than the American ones and yield almost twice the quantity of oil. After a short while, the American plants had been replaced almost completely by the English ones, and only in the neighbourhood of Charlotte in the State of Michigan, there are still some plantations of the pure American variety. The bad yield in oil indicates at once where both varieties are mixed. The cultivation of peppermint in Wayne County (New York) has ceased altogether.

According to Magnus, Mabee and Reynard, Inc.[1]) the peppermint oil of the last crop shows an exceptional rotatory power (α_{D20} — 17 instead of — 23°) and contains but little menthol.

E. R. Kremers[2]) obtained by cohobation of the watery distillate of American *Mentha piperita* three fractions of the following properties: — d_{240} 0.916 to 0.940, n_{D240} 1.468 to 1.476, ester v. 21.65 to 29.9, ester content 7.7 to 10.6 per cent., alcohol as ester 6.0 to 8.3 per cent., ester v. after acetylation 195 to 160.5, total alcohol 63.6 to 50.8, free alcohol 57.6 to 42.5 per cent. The chief components were menthol (preparation of pure menthol, without any indication of the constants) and menthone (semicarbazone, m. p. 185°. Menthyl ester and 1,3-methylcyclohexanone (b. p. 169°, d_{210} 0.915, n_D 1.4430, semicarbazone, m. p. 180°) were present in small quantities.

As to the history of peppermint oil in America, see page 105 of this *Report*.

Peppermint Oil, Italian. — G. Micheletti[3]) communicates that this year's peppermint crop in Italy (Vigone, Pancalieri, Piemonte) is satisfactory. 30000 kilos of oil were obtained, a quantity superior to last year's result. The quality was also better. The menthol content exceeded 50 per cent. on an average.

Peppermint Oil, Japanese. — The lack of demand, characteristic of the Japanese peppermint market during the first months of the year covered by this *Report*, would certainly have lead to a reduction of the prices in the course of the summer, if not speculators had done everything to hold them and even send them up, if possible, by means of extensive advances of money granted by the banks. They succeeded in bringing about a temporary firmness of the market in autumn, but under the influence of the new crop and the considerable old stocks the opinion seems to prevail in the quarters concerned that a fall of the prices is not improbable in the near future, unless unforeseen events prevent it. The stocks in Japan about the middle of February

[1]) *Oil, Paint and Drug Reporter* **100** (1921) N⁰ 17, 31. — [2]) *Journ. Americ. Pharm. Assoc.* **10** (1921), 835. — [3]) *Parfum. moderne* **14** (1921), 215.

Distillation of Peppermint Oil in Japan.

(After a water-colour painting in the possession of the Perfumery Department of the German Museum in Munich. Gift of the firm of Schimmel & Co.)

| 1910 | 1911 | 1912 | 1913 | 1914 |

Produzierte Menge in Kin	Preise in		1915	1916	1917	1918	1919	1920
	£	Yen						
	£ s. d	Yen						
3.700.000	4. 9. 5	37.00						
		.75						
		.50						
3.800.000	4. 7. 0	36.00 .25						
		.75						
		.50						
3.500.000	4. 4. 7	35.00 .25						
		.75						
		.50						
3.400.000	4. 2. 2	34.00 .25						
		.75						
		.50						
3.300.000	3.19. 9	33.00 .25						
		.75						
		.50						
3.200.000	3.17. 4	32.00 .25						
		.75						
		.50						
3.100.000	3.14.11	31.00 .25						
		.75						
		.50						
3.000.000	3.12. 6	30.00 .25						
		.75						
		.50						
2.900.000	3.10. 1	29.00 .25						
		.75						
		.50						
2.800.000	3. 7. 8	28.00 .25						
		.75						
		.50						
2.700.000	3. 5. 3	27.00 .25						

Fluctuations of **Menthol prices** . . . . . = blue line
– – **Peppermint oil prices** = red line
from 1901 to 1914[1]
calculated in *L. s. d.* and *Yen* per kin.

○ : nominal quotations.
● : actual business transactions.
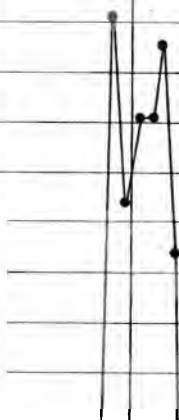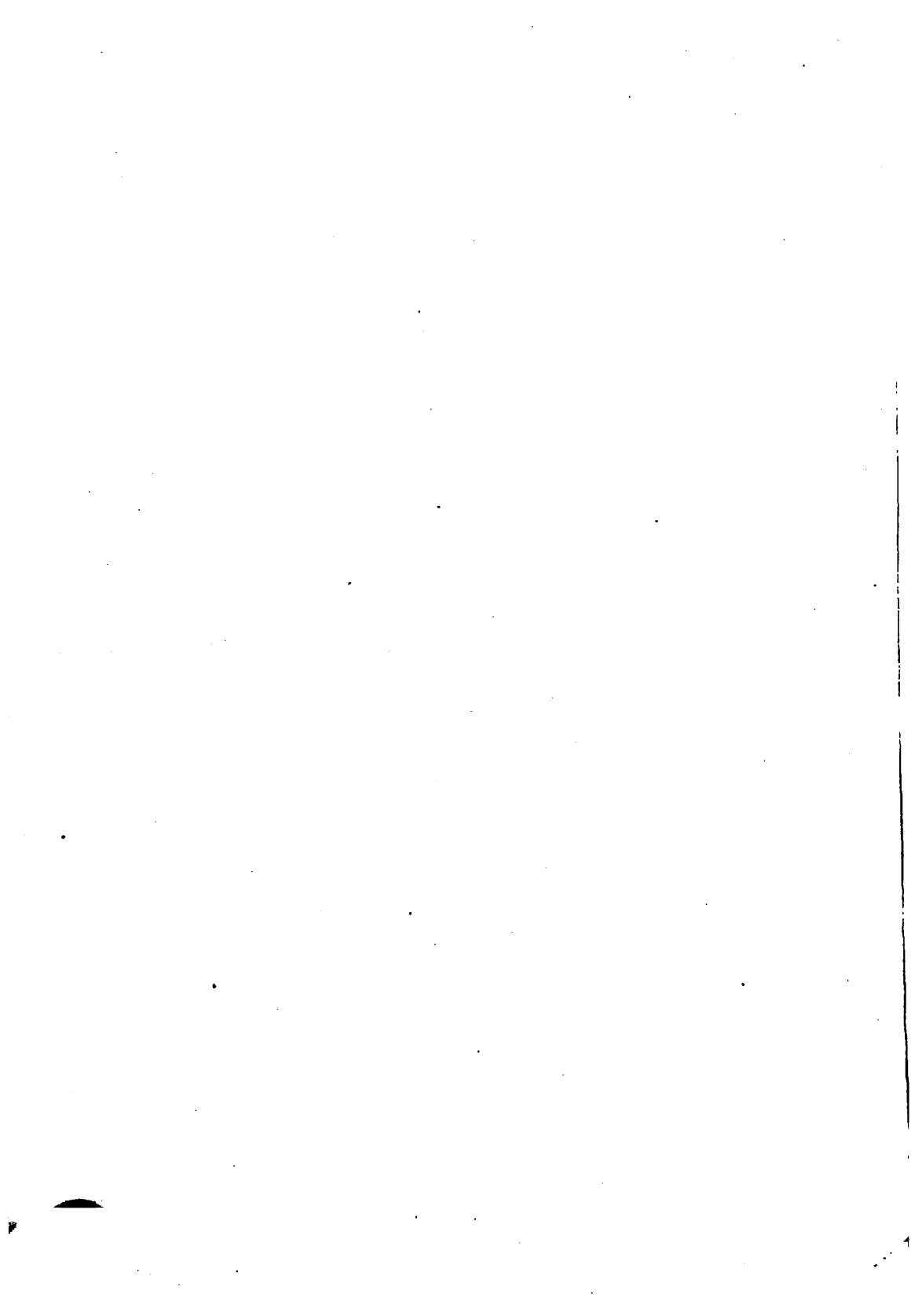
are said to have been 6200 cases of menthol and 7100 cases of peppermint oil, so that it seems to be only a question of time when the holders will come down with their prices, in order to revive the demand. The Japanese refiners also keep back with their purchases of crude oil, limiting themselves, as it seems, to satisfy what little demand there may be out of their old stocks. The quantities mentioned above represent about 700000 lbs. of oil, to which the rather considerable stocks in London, New York and Hamburg have to be added. It has generally been possible of late to buy much cheaper in London than in the producing country.

The Japanese export statistics, rectified of late, give the following figures for the last 13 years:—

	Peppermint Oil							Menthol						
1909	151 800	kin	to	the	value	of	Yen	466 600	102 400	kin	to	the	value	of	Yen	490 500
1910	146 200	„	„	„	„	„	„	464 500	116 900	„	„	„	„	„	„	648 800
1911	172 400	„	„	„	„	„	„	625 600	113 600	„	„	„	„	„	„	963 200
1912	184 900	„	„	„	„	„	„	699 300	133 200	„	„	„	„	„	„	1 589 700
1913	282 100	„	„	„	„	„	„	1 017 700	232 900	„	„	„	„	„	„	2 872 800
1914	277 760	„	„	„	„	„	„	818 800	269 300	„	„	„	„	„	„	1 816 100
1915	341 200	„	„	„	„	„	„	697 400	323 500	„	„	„	„	„	„	1 851 000
1916	360 700	„	„	„	„	„	„	844 500	386 500	„	„	„	„	„	„	2 410 600
1917	259 700	„	„	„	„	„	„	593 600	251 200	„	„	„	„	„	„	1 594 300
1918	214 700	„	„	„	„	„	„	539 700	237 500	„	„	„	„	„	„	1 554 000
1919	409 199	„	„	„	„	„	„	1 307 113	239 973	„	„	„	„	„	„	2 546 898
1920	321 300	„	„	„	„	„	„	1 848 000	363 400	„	„	„	„	„	„	5 417 000
1921	245 400	„	„	„	„	„	„	558 413	229 900	„	„	„	„	„	„	2 172 480

The diagram here inserted has been sketched and kindly placed at our disposal by Mr. K. Kobayashi. It gives an idea of the prices paid for menthol and peppermint oil in the years from 1901 to 1920. The blue dots represent the menthol, the red ones, the peppermint oil; "o" means nominal quotation, no business having been done at the figure, whereas in the cases marked "●" actual sales resulted.

Specially striking in the diagram are the periodical rises of the quotations for peppermint oil in the years 1902/03, 1912/13 and 1919/1920, which did not last very long, however. Whereas the high prices of 1902/03 were due to precipitated purchases of the American Government[1]), those of 1912/13 to the bad crop[2]), the last quite extraordinary rise can only be looked upon as a consequence of the war.

R. E. Kremers[3]) investigated the oil obtained through cohobation of the distillation water of the Japanese peppermint. It had the following properties:— d_{18^o} 0.938, n_{D18^o} 1.485, ester v. 39.2, ester v. after acetylation 69.1, ester content 13.8 per cent., alcohol as ester 10.9, total alcohol 20.3, free alcohol 9.4 per cent. It was impossible to establish the presence of menthol, whereas the fractionated distillation yielded a product composed almost entirely of pulegone (nitroso derivative, m. p. 83°, semicarbazone, m. p. 167°).

Pimento Leaf Oil. — On page 76 of our last *Bericht* (German), we quoted a communication from an English source, according to which it was possible to obtain 100000 lbs. of pimento leaf oil annually in Jamaica. The original paper[4]) now before

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[1]) Comp. *Report* April 1903, 60. — [2]) *Ibid.* April 1912, 99. — [3]) *Journ. Americ. Pharm. Assoc.* 10 (1921), 834. Comp. also the water oil of the American peppermint and of *Monarda fistulosa*, pages 58 and 50 of this *Report*. — [4]) *Commerce Reports*, No 257 of November 1st, 1920.

us states that the trials of preparing oil from the leaves are still going on in the Government Laboratories of Jamaica. The production on a large scale was not yet possible. It is further said that experiments had shown the pimento leaf oil to contain 1.8 per cent. eugenol, from which it would be possible to prepare to advantage *iso*eugenol and vanillin.

Pine Needle Oils. — A comparative investigation of Eastern and Western hemlock oils has been started by D. E. Cable[1]. Five oils originating from the East (Michigan, Wisconsin, New Hampshire, Tennessee, Virginia) which were distilled during the months of June, July, and August from the stripped leaves of *Tsuga canadensis*, Carr. with a yield of 0.29 to 0.65 per cent., showed the constants: — $d_{15^0}^{20^0}$ 0.9020 to 0.9234, $[\alpha]_{D20^0}$ — 14.80 to — 21.65°, n_{D20^0} 1.4691 to 1.4704, acid v. 0.33 to 0.70, ester v. 103.8 to 147.35, ester v. after acet. 113.5 to 171.94, esters calc. as bornyl acetate 36.33 to 51.57 per cent., total borneol 31.24 to 47.41. The Wisconsin oil excelled by its high content of esters and of total borneol.

Three oils from Western hemlock, originating from Coeur d'Alene, Idaho, behaved quite differently. They were distilled in the months of May, June, and July 1920 from the stripped leaves of *Tsuga heterophylla*, Sargent (yield 0.32 to 0.36 per cent.) and showed the constants as follow: — $d_{15^0}^{20^0}$ 0.8444 to 0.8521, $[\alpha]_{D20^0}$ — 6.74 to — 20.00°, n_{D20^0} 1.4790 to 1.4840, acid v. 2.57 to 3.4, ester v. 6.7 to 17.25, ester v. after acet. 19.6 to 33.4, esters calc. as bornyl acetate 2.35 to 6.02 per cent., total borneol 5.43 to 9.24 per cent.

For the purpose of comparing these oils with ordinary commercial hemlock oils of the years 1909 and 1919, the following constants for three oils of commerce were ascertained: — $d_{15^0}^{20^0}$ 0.9190 to 0.9664, $[\alpha]_{D20^0}$ — 14.85 to — 24.85°, n_{D20^0} 1.4721 to 1.4786, acid v. 1.51 to 18.45, ester v. 105.09 to 115.41, ester v. after acet. 149.51 to 150.83, esters calc. as bornyl acetate 36.78 to 40.39 per cent., total borneol 41.55 to 41.74 per cent.

The last-named oils are remarkable on account of the extraordinary high upper values for density, refractive index, and acid content indicating, partially, resinification.

The essential oil of the needles from *Pinus silvestris*, L. of Russian origin has hitherto been investigated only by Hirschsohn[2] and, later on, by J. Schindelmeiser[3]. According to this author, Russian pine needle oil constitutes an oil with a pleasant aromatic odour, showing the constants: — b. p. 160 to 250°, d_{180} 0.875, $\alpha \pm 0$. On fractionated distillation from 10 to 10° the following fractions resulted: — 160 to 170°, 48 per cent.; 170 to 180°, 32 per cent; 180 to 190°, 12 per cent. The first fraction was optically active ($\alpha_D + 2°30'$) and contained *d*-pinene; nitrolamine, m. p. 118°. The fraction 170 to 180° was lævorotatory ($\alpha_D - 2°46'$) and contained, in the opinion of the author, equally as the fraction 180 to 190°, *l*-limonene in addition to some *d*-limonene (tetrabromide of the total limonene, m. p. 125 to 126°, dihydrobromide of the total limonene, m. p. 64°; cf. the constants of the corresponding dipentene derivatives). The fraction boiling above 190° contained inactive borneol (phenyl-urethane, m. p. 137 to 138°) and, probably, some cadinene (dihydrochloride, m. p. 117 to 118°). Hence, the oil resembled in its composition, apart from the absence of sylvestrene, the German and the Swedish pine needle oils[4].

Quitch Root Oil. — It is little known that quitch root (*Triticum repens*, L.) contains an essential oil. A trial distillation of selected roots from Miltitz fields yielded

[1]) *Journ. Americ. pharm. Assoc.* 10 (1921), 170. — [2]) *Pharm. Zeitschr. f. Russland* 481 (1891). — [3]) *Sitz.-Ber. d. Naturforscher-Ges. b. d. Universität Jurjew (Dorpat)* 13, 2 (1903), 315. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 122 and *Bericht* (German) 1920, 35.

0.0065 per cent. of a dark brown distillate of feebly aromatic, somewhat sweetish odour; d_{16^o} 0.9665, acid v. 36.2, ester v. 29.0, incompletely soluble in 10 vols. of 80 per cent. alcohol. Rotation and refraction could not be determined on account of the dark colour of the oil.

Another batch of quitch roots, mixed with tarragon roots, however, yielded 0.052 per cent. of essential oil of light brown colour: — d_{15^o} 0.9670, α_D +2° 30', n_{D20^o} 1.55359, acid v. 5.4, ester v. 10.6, incompletely soluble in 10 vols. of 80 per cent. alcohol, soluble in 2 vols. and more of 90 per cent. alcohol.

Ravensara Oil. — The leaves and young twigs of *Ravensara aromatica*, J. F. Gmel., a lauracea growing on the high plains of Madagascar, yielded on distillation with steam an essential oil of an agreeable, camphor-like smell. It reminded one of eucalyptus oil and consisted, according to Ferrand and Bonafous[1], of a terpene mixed with an oxygenated body.

Roman Chamomile Oil. — According to Massera[2], the oil contained in the flowers of Roman chamomiles to the extent of 0.8 to 1 per cent. had the following constants: — d 0.905 to 0.920, $[\alpha]_D$ — 3° to +3°, sap. v. 220 to 320, soluble in less than 1 vol. and, with slight turbidity, in 3 vols. of 70 per cent. alcohol. In addition to the components enumerated by the author (*iso*butyl and *iso*amyl esters of angelic and tiglic acid, anthemol and anthemene), azulene is present, besides, according to Blaise, *n*-butylic alcohol and, according to van Romburgh, also *β*-methylethylpropylic alcohol[3].

Rose Oil, Bulgarian. — The estimations of the 1921 crop vary between 1200 and 1500 kilos. Although these quantities do not come up by for the average pre-war results, they are about 20 per cent. better than last year's result. This excess has not had any effect on the prices, however, and the market remained almost unaltered. It was remarkable to what an extent the illegitimate trade with rose oil has grown. It is understandable that the important banks are greatly interested in transactions concerning such a valuable commodity and that even the State may now and then sell certain important lots, last year, however, rose oil was offered from many other quarters, which have but little or nothing at all to do with the distillation of otto of roses. The number of such sellers, who often carried their goods about with them in handbags, was specially large, among them a good many Bulgarian students, who meant to earn like that the means necessary for continuing their studies at German universities. It is desirable that these after-effects of the war should disappear quickly, to the benefit of the legitimate trade. Many a buyer who was not in a position to test the "bargain" offered, has been done in such transactions.

T. H. Shipkoff[4] publishes an article on the Bulgarian rose industry, from which we copy some data, as far as they are not contained in our previous *Reports*[5]. The district in Bulgaria, called by all western travellers "The Land of the Roses", extends over that portion of the southern slopes of the main Balkans mountains, which comprises the whole branch range of Stredna Gora (Little Balkans). Its average length is about 80 miles and its average with about 30 miles[6]. The average elevation of the rose district is bout 1300 feet above the level of the sea, and the average height of the

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[1] *Parfum. moderne* 14 (1921), 100. — [2] *Rev. Ital. d. Essenze e Profum.* As per *Perfum. Record* 12 (1921), 283. — [3] Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 616. — [4] *Americ. Perfumer* 16 (1921), 48. — [5] Comp. *Reports* April 1908, 86; April 1913, 89; 1916, 47. — [6] Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 552, map.

main Balkans in the north is about 5600 feet, while the average height of the Little
Balkans is about 3700 feet. There are over 180 communities or villages with more than
21 000 small proprietors of rose gardens owning on an average about one acre each. Only
about half of the 14 000 small native stills, existing in the country, are still in use, for
during the last years before the great war, 12 modern distilling plants have been built.

Whereas this industry had developed steadily up to the Balkan war in 1912, it
decreased continuously from that time. The consequences of the hard years of war
are still felt and other agricultural products have taken the place of the roses, although
the demand for otto of roses has trebled of late. From 1889 to 1912 the area planted with
roses increased from 7500 to 30 000 acres, yielding on an average up to 27 000 000 lbs. of
roses, from which 3600 to 4000 kilos of rose oil were obtained. The record crops of 1900 and
1907 yielded even 30 000 000 lbs. of flowers each, or about 175 000 ounces of otto of roses.

The present area cultivated with roses will hardly exceed 14 000 acres and the yield
of oil has also gone down, as the rose gardens have been neglected and not sufficiently
manured. The quantity of oil produced went down from 4000 kilos in 1912 to 2410 kilos in
1917, 1840 in 1918, 1600 in 1919, 1200 in 1920[1]) and for 1921 only 1000 kilos are expected.

Prior to the war, the exports were as follows: —

Destination	1900	1906	1911
France	1548 kilos	2607 kilos	1483 kilos
United States . . .	849 „	1524 „	525 „
Germany	568 „	1113 „	1595 „
Great Britain . . .	1175 „	1074 „	572 „
Russia	202 „	278 „	158 „

During the war, nothing was exported to the United States, France, England and
Russia, whereas Germany imported annually 1700 kilos, Switzerland about 600 kilos,
Austria about 200 kilos, together with Holland. Since the war is over, the American
market has been the most important by far. In 1919, 3500 kilos were exported to the
United States, 900 kilos to France and 400 kilos to England[2]). The exports to Germany
are supposed to have risen considerably in 1920.

Rosemary Oil. — On Spanish oil of rosemary, see page 106 of this *Report*.

Sandalwood Oil, East Indian. — The Department of Statistics in India publishes
the following statement showing the exports of sandalwood oil[3]): —

Countries of final destination	January 1921. Quantity	January 1921. Value	Ten months, April 1920 to January 1921. Quantity	Ten months, April 1920 to January 1921. Value
Great Britain	6237 lbs.	155 925 Rs.	109 652 lbs.	2 745 600 Rs.
France	2930 „	69 000 „	5030 „	125 000 „
Straits Settlements . . .	—	—	190 „	2300 „
Ceylon	—	—	4 „	275 „
Hong Kong	720 „	4320 „	1290 „	8880 „
Asiatic Turkey	—	—	—	15 „
Java	—	—	980 „	20 300 „
Portuguese East Africa .	—	—	2 „	40 „
Egypt	—	—	1190 „	32 825 „
Australia	—	—	100 „	2150 „
Total	9887 lbs.	229 245 Rs.	118 438 lbs.	2 937 385 Rs.

[1]) It is stated officially that the 1920 crop yielded only 900 kilos, comp. *Bericht* (German) 1921, 39. —
[2]) These figures, compared with those given for the actual production of rose oil, confirm the well-known fact that
Bulgarian Otto of Roses is exported only with the usual addition of palmarosa oil. — [3]) *Perfum. Record* 12 (1921), 180.

In the report on the Administration of Mysore[1]) for the year ending June last, it is stated that the sandalwood oil factories dealt with 1362 tons of sandalwood. The demand for the oil was good, but the profits were small, as the prices of the wood had been driven up very high in the Coorg and Madras auctions.

As the Dutch East Indies export sandalwood and on the other hand import about 1000 lbs. of sandalwood oil annually from British India, the Government intends to produce it in the country. A question still to be solved would be the cutting of the wood into chips, in which direction experiments are going to be made. Out of 37 kilos of sandalwood 1023 cc. = 2.6 per cent. of oil have been distilled[2]). The plan seems to have come to nothing, however, for according to a report of the Dutch Chamber of Commerce in New York[3]) the distillation of sandalwood oil in Java, begun during the war, has been given up again, as being unprofitable.

E. J. Parry[4]) communicates that during the last years he frequently received from reliable French or English (Indian) distillers sandalwood oils which were fit for use in perfumery but the constants of which did not comply with the requirements of the British Pharmacopeia. In his opinion, the distillation in such cases had either been incomplete or too slow. Parry proves experimentally that a prolonged action of steam on the oil altered the constants, reducing in particular the optical rotation.

We would add that this is nothing new, for we have pointed out years ago[5]) that the decomposition products, which easily form during the distillation, alter the properties of the oils and that only a very careful distillation will yield a normal product.

Sandalwood Oil, West Indian. — Large quantities of wood have arrived of late and we hope to be able before long to supply fresh oil on a larger scale.

Oil of Satureia montana. — By steam-distillation of the not yet flowering dry herb of *Satureia montana*, L., gathered in June in the Italian province of Aquila, P. Leone and E. Angelescu[6]) obtained 0.69 per cent. of a yellow of strong aromatic smell and burning taste. By extraction of the herb with acetone and distillation of the extract with steam, the authors obtained 1.63 per cent. of an oil which had the same specific gravity and the same phenol content as the former. It is to be supposed, in consequence, that the dry herb contains in realty at least 1.63 per cent. of oil. — The oil had the following properties: — d_{40}^{25} 0.9053, $[\alpha]_{D17^\circ}$ — 3.05°, n_{D16° 1.49926, acid v. 2.22, sap. v. 6.75, ester v. 4.53, corresponding to an ester content of 1.58 per cent. (calculated as linalyl acetate), carvacrol content 28 per cent. (nitroderivative, m. p. 77 to 78°; determined through shaking with a 5 per cent. soda lye). The oil freed from the phenol contained 10 per cent. of an alcohol, which has not been identified more closely (sap. v. after acet. 54.3) and yielded the following fractions on repeated distillation under normal pressure: — 1. b. p. 170 to 180° (54 per cent.), 2. b. p. 180 to 190° (12 per cent., 3. b. p. 190 to 205° (8 per cent.), 4. b. p. 205 to 232° (6 per cent.), 5. b. p. 232 to 252° (12 per cent.). After having been boiled for five hours with metallic sodium, the first and second fractions yielded other fractions boiling at 173 to 175° (38.1 per cent.) and at 176 to 178° (20.3 per cent.), consisting of cymene (hydroxy*iso*propylbenzoic acid, m. p. 156 to 157°) and dipentene

[1]) *Americ. Perfumer* **16** (1921), 107. — [2]) *Chemist and Druggist* **94** (1921), 406. — [3]) *Holland and her colonies* **1** (1921), No. 7, p. 15. — [4]) *Parfum. moderne* **14** (1921), 54. — [5]) Comp. *Report* April 1908, 92. — [6]) *Gazz. chim. ital.* **51** (1921), II. 368.

(nitrolbenzylamine, m. p. 108°), respectively. The original oil, therefore, contained abou 27 per cent. of cymene and 14 per cent. of dipentene.

The oil of the French plant has been investigated already years ago by several authors. A. Haller found in it 35 to 40 per cent. of carvacrol. According to our determinations an oil from Barrême contained about 27 per cent. and one from Sault about 32 per cent. of carvacrol[1]).

Oil of Skimmia laureola. — The oil of *Skimmia laureola*, Hook. fil., on whose origin and properties we gave a short notice p. 46 on of our last *Bericht* (German ed.), has recently been investigated by J. L. Simonsen[2]). On distilling the shade-dried leaves collected in the Chakrata Division during June and early July, the author obtained about 0.5 per cent. of a pale emerald-green oil with the following constants: $d_{20°}^{20°}$ 0.9041; $n_{D20°}$ 1.4648; acid v., 3.63; sap. v. 197.36; sap. v. after acet. 238.6 (prior to acetylation the oil was mixed with turpentine oil)[3]). After washing the oil with dilute alkali, the oil was repeatedly fractionated under 200 mm. pressure and the following fractions were obtained: — 1. B. p. 130 to 140°, 0.46 per cent.; 2. 140 to 145°, 4.6 per cent.; 3. 145 to 150°, 0.61 per cent.; 4. 150 to 155°, 8.4 per cent.; 5. 155 to 160°, 2.3 per cent.; 6. 160 to 167°, 2.0 per cent.; 7. 167 to 173°, 50 per cent.; 8. 173 to 177°, 0.61 per cent.; 9. 177 to 182°, 1.05 per cent.; 10. 182 to 190°, 1.2 per cent.; 11. above 190°, 18.2 per cent.

The first three fractions contained a hydrocarbon boiling at 130 to 135° (200 mm.) or 176 to 182° (695 mm.); $d_{20°}^{20°}$ 0.859; $[\alpha]_{D20°}$ — 4.11°; $n_{D20°}$ 1.471), the nature of which remained undecided. Fraction 4 consisted of nearly pure *l*-linalool (phenylurethane, m. p. 65°). The fractions 5 to 9 contained partly *l*-linalool, partly *l*-linalyl acetate, partly a mixture of both. In addition, fractions 8 to 10 contained a high-boiling alcohol. From fraction 11, repeated distillation yielded unpleasently-smelling oils, possibly mixtures of sesquiterpene alcohols and esters.

Hence, the oil investigated consisted in the main of *l*-linalyl acetate, furthermore of *l*-linalool, a hydrocarbon and a mixture of sesquiterpene alcohols and esters.

Spearmint Oil. A sample of the entire dried plant of *Mentha longifolia* (Host, or Huds.?) collected in the Somerset East district of the Cape Province and consisting of leaves 40 p. c., and loose stalks 60 p. c., was examined at the Imperial Institute[4]) The stalks were found to be practically free from volatile oil, the leaves yielded on steam distillation 2.4 per cent. oil, equivalent to a yield of 0.98 per cent. from the entire original sample. The colourless oil had the characteristic odour and taste of spearmint oil and the following constants:—$d_{15°}^{15°}$ 0.947; α_D — 47.6°; n_D 1.4925; ketones (estimated by sulphite method), calculated as carone, 70 per cent. The oil from this sample of spearmint resembled the oils from *Mentha spicata*, Huds. and of *Mentha viridis*, L., but contained a very high percentage of ketones and corresponded in this respect with the Austrian spearmint oil.

Spike Oil. — As to Spanish spike oil, see page 106 of this *Report*.

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 470. — [2]) *Journ. Soc. chem. Ind.* 40 (1921), T. 126. — [3]) The above constants differ considerably from those found by Roure-Bertrand Fils (comp. *Bericht* 1921, p. 46). With a leaf oil forwarded to us we ascertained the following characters: — $d_{15°}$ 0.8876, $\alpha_D + 2°22'$, $n_{D20°}$ 1.47260, acid v., 0, sap. v., 128.8 = 45.1 per cent. of esters, calculated as linalyl acetate; soluble in 0.2 vol. 90 per cent. alcohol, with more than 1.3 vol. strong opalescence. The colourless oil showed a bluish fluorescence and recalled the odour of petitgrain oil. It was said to originate from *Skimmia laureola*, Sieb. et Zucc. (*Limonia laureola*, D.C.), Roure-Bertrand Fils state *Skimmia laureola*, Hook. fil., which name we fail to find in the *Kew Index*. — [4]) *Bull. Imp. Inst.* 18 (1921), 350.

Distillation of Essential Oils in Spain.
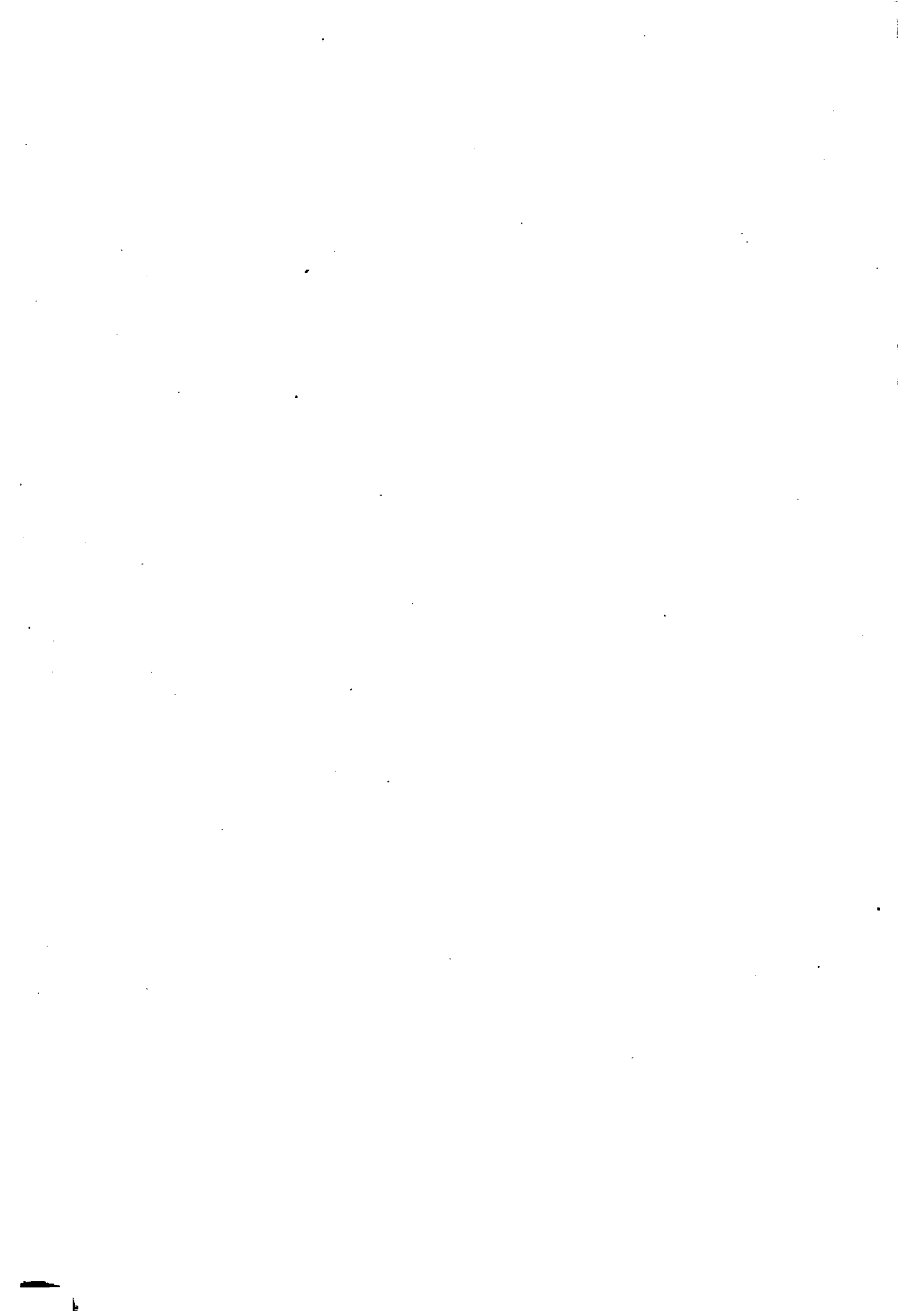
Staranise Oil. — The following statistics of maximum and minimum prices of staranise oil are taken from an English periodical[1]): —

	Maximum	Minimum		Maximum	Minimum
1911	6/0	4/9	1916	3/6	3/2
1912	6/11	5/6	1917	4/6	3/3
1913	7/3	6/3	1918	6/2	4/0
1914	6/3	5/0	1919	6/0	4/2
1915	4/9	3/0	1920	6/0	3/6

As it is shown, the maximum pre-war prices have not been reached again, in spite of the universal depreciation of the money. Although in November 1921 the price went down as far as 2/2 per lb.[2]), it was believed that this was not the lowest yet, for there were considerable stocks and little demand. In 1921, 4000 cases of $66^2/_3$ lbs. each arrived in London, where abundant stocks existed already. The oil was imported partly in exchange for textiles.

It is further stated that formerly there was a good market for staranise oil, chiefly for liqueurs and confectionery. Nowadays the Russian demand is missing and France, Germany and the United States require but little. In the latter country, the decrease in the demand for staranise oil is ascribed to the prohibition of alcoholic drinks. The best consumers of the articles are now most likely Spain and South America, but it is expected that the French and English demand will increase again.

Oil of Tagetes anisata. — The fresh herb of *Tagetes anisata,* Lillo, *n. sp.,* a composita growing in the pampas of Argentina at an elevation of from 1000 to 3000 m., yielded on steam distillation, according to F. Zelada[3]) 0.7 to 0.8 per cent. of a green oil. The product resembled anise oil and had the following properties: b. p. 214 to 218°, solidification p. — 6°, d_{150} 0.9862, α — 1°10', n 1.5432, ester v. after acetylation 23.4, sap. v. 3.1, iodine v. 158.5, alcohol as $C_{16}H_{18}O$ 0.852 per cent., ester as $C_{16}H_{17}OCOCH_3$ 1.082 per cent., total alcohol as $C_{16}H_{18}O$ 3.229 per cent., soluble in 5 vols. of 90 per cent. alcohol[4]).

Tarragon Root Oil. — See Estragon root oil, p. 34 of this *Report.*

Thyme Oil. — The Spanish oils of thyme are of different composition and may be grouped in oils containing thymol, carvacrol, or citral. The same division could be used for the manifold species of *Thymus* occurring in Spain. According to the few existing authentical indications concerning the botanical origin of the Spanish thyme oils, there seems to be a certain conformity in the characteristics of the plants belonging to one and the same of the groups mentioned. According to Rubeck and E. H. Holmes[5]), *Thymus vulgaris,* L., and *Thymus Zygis,* L., which are much alike and are both known in Spain by the name of *tomillo salsero,* being used as pot-herbs, certainly belong to the first group. *Thymus hyemalis,* Lange, according to Holmes the mother-plant of the so-called Spanish verbena oil, is closely allied to *Thymus hirtus,* Willd. *(tomillo limonero);* both kinds contain citral[6]). The similarity appears to be less striking (the relative indications in books, etc. are very scanty) between *Thymus Mastichina,* L., *(tomillo blanco)* and *Thymus cephalotus,* L., the oils of which according to Dorronsoro[7])

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[1]) *Chemist and Druggist* 95 (1921), 631. — [2]) *Com. Bericht* (German) 1921, 46. — [3]) *Parfum. moderne* 14 (1921), 32. — [4]) There seem to be grave discrepancies between the acetylation and ester values and the amount of alcohol, etc. calculated. Besides, $C_{16}H_{18}O$ seems to stand for $C_{10}H_{18}O$. — [5]) *Perfum. Record* 11 (1920), 339. — [6]) Cf. *Bericht* (German) 1921, 87. — [7]) *Comp. Report* April 1911, 111.

contain about 60 per cent. of cineole. We do not know, however, what variety of *Thymus* plants contain the oils rich in carvacrol. Holmes may be right in saying that *Thymus Piperella*, L., and *Thymus cæspiticius*, Hoffm., the popular name of which *(pebrella)* indicates a sharp taste like pepper, belong to the carvacrol group. An oil distilled from the fresh herb of *Thymus capitatus*, Lk. (from Granada) contained according to our own investigation 6 per cent. of thymol and a liquid phenol, perhaps carvacrol[1]).

This is about all that has been recorded as to the exact botanical origin of the Spanish thyme oils. On the other hand it is known that more than 30 (Willkomm[2]) states 39) different kinds of *Thymus* are spread over the Iberian peninsula. They partly grow in one and the same district, have great similarity and are perhaps not always differentiated by the gatherers. The thyme plants are gathered above all from the *"tomillares"* (*tomillo* = thyme) which are so characteristic for Spain and, with exception of the Northatlantic zone of the peninsula, occur in the central table-land as well as in the coast provinces and the lowlands along the Ebro, in South Aragon, Catalonia, Valencia, lower Andalusia and Algarbia, covering enormous spaces of uncultivated land. These *"tomillares"* attain their largest dimensions in the table-land, along the Duero, on either side of the central mountain chain and in the East, South and South-West of New Castile. There are thyme, lavender, sage and rosemary heaths, named after the labiate that preponderates. C. Hartwich[3]) gives a very good description of such a heath: — "On this waste ground of débris the plants grow isolated, though fairly close together, so that the naked soil can be seen everywhere in between. This is the reason why such stretches of land often appear absolutely bare from a distance. The dominating plants, as the name of the steppe indicates already, is a species of thyme (*Thymus Zygis*, L.). The plant forms round little shrubs, perhaps as large as a fist, sometimes, when a stem grows a little higher, miniature trees, like those we owe to the Japanese art of gardening. They have small, needle-shaped leaves, on which the golden-yellow oil glands can be seen through a magnifying glass, and are covered with tiny red flowers. A stem which I examined at home was nine years old."

The *Thymus* species most frequently named and apparently also the most widely distributed in Spain are *Thymus vulgaris*, L., *Thymus Zygis*, L. and *Thymus Mastichina*, L. As E. M. Holmes[4]) determined, *Thymus Zygis* differs from the otherwise similar common thyme, as follows: — The bracts are larger than the ordinary leaves, the whirls of whitish flowerets from an uninterrupted spike and no axillary or terminal heads as with *Thymus vulgaris*. According to Willkomm[5]) the common thyme is to be found in Navarra, in the plain of Pamplona, along the Duero and the Iberian central mountain chain, in the Nord-West of Guadalajara and in the mountainous regions of Catalonia and Valencia, whereas *Thymus Zygis* occurs in the North of Old Castile, near Alar del Rey (Palencia) in the upland ol Murcia in New Castile, in the Vega of Granada, in the Sierra Nevada and in the uncultivated coast regions of the provinces of Cadiz and Huelva. — *Thymus Mastichina* grows on waste ground and by the side of paths and fields in Cantabria, in the slate mountains of Asturia and Leon, in the northern table-land (together with *Thymus vulgaris*), in the lavender heaths of New Castile along the central mountain chain (together with *Thymus Zygis*), on sandy soil between Almeria and the Bay of Gibraltar, on the dry calcareous hills round Granada, and in the *"tomillares"* of the coast zone of Cadiz and Huelva (together with *Thymus Zygis*). Of

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[1]) *Bericht* October 1889, 56. — [2]) Engler, *Die Vegetation der Erde. Grundzüge der Pflanzenverbreitung auf der iberischen Halbinsel.* By R. Willkomm. 1896. — [3]) Spring holidays in Spain. *Apotheker-Ztg.* 21 (1906), 842. — [4]) *Loc. cit.* — [5]) *Loc. cit.*

the other species the following are mentioned:— *Thymus hirtus*, Willd., which thrives in Central and southern Spain, on the calcareous hills round Granada and in the lower regions of the Pinsapo Forest, *Thymus hyemalis*, Lange, in south-eastern Spain, *Thymus cephalotus*, L., in Valencia, in lower Asturia and, according to Dorronsoro[1]) in Almeria, *Thymus cœspiticus*, Brot., in Estremadura and Galicia, *Thymus Piperella*, L., in Valencia on rocky slopes, *Thymus cerpylloides*, Bory, *(Samarilla)* in the alps of the Sierra Nevada.

To quite another species belongs the so-called Andalusian thyme *(Tomillo andaluz = tomillo carrasqueno)* or *Corydothymus*, which according to Blas Lazaro[1]) is *Corydothymus capitatus*, Rchb. B. Dorronsoro[2]) writes about it as follows:—"Various kinds of thyme are distilled in Spain, viz., the *tomillo corriente* (common thyme) = *tomillo aceitunero* (olive thyme) = *Thymus vulgaris*, L., the *tomillo risquero* (thyme of the rocks) = *Thymus Zygis*, L., the *tomillo sanjuanero* (St. John's thyme) = *Thymus hyemalis*, Lg., and the *tomillo carrasqueno* (holm-oak thyme) or *tomillo andaluz* (Andalusian thyme), which latter, however, is no real thyme, but *Corydothymus capitatus*, Rchb., belonging to an allied species."

In August 1915, we examined in our research laboratory a Spanish oil from Barcelona, on whose botanical origin, unfortunately, nothing definite could be ascertained. Since, only very little positive is known as to the chemical composition of the Spanish oils, the results of the following investigation gave no clue concerning the botanical source of the oil. Owing to the war, the work had unfortunately to be discontinued and was terminated only before long, when the oil had been left standing for nearly six years (protected from direct light) after having been fractionated and freed from phenols by treatment with dilute caustic lye.

The original oil showed the following constants:— d_{15^o} 0.9297, $\alpha_D +0^o 35'$, soluble in 3.5 vols. and more of 70 per cent. alcohol; phenols 45 per cent., for the greater part thymol.

The most volatile fraction of the b. p. 130 to 132° smelled of *amyl alcohol* and gave the characteristic naphthylurethane, m. p. 51 to 52° obtained by us on a previous occasion. In the fractions of b. p. range 132 to 150° we suspected owing to their amylaceous smell the presence of *amylcarbinols*. Since they consisted doubtlessly of mixtures, contaminated possibly with small amounts of amylic or similar ketones, we refrained from further isolation and identification. We only by way of experiment, succeeded in isolating a naphthylurethane, m. p. 47 to 48°. We were unable to prove the existence of a ketone, nor the formation of such by oxidation with bichromate solution. A small fraction, b. p. 145 to 150° (d_{15^o} 0.8495, $\alpha_D +3^o 28'$, n_{D20^o} 1.45052), yielded on benzoylation with the aid of pyridine a benzoate, b. p. 134 to 135° (6 mm.), which on saponification gave rise to an alcohol with the characteristic odour of *β,γ-hexenol*. This alcohol had previously[3]) been obtained by us in shape of its phenylacetate from the last runnings of Japanese peppermint oil. Although the oil showed the same boiling point (156°) as the above-mentioned alcohol, we were unable to raise the melting point of the naphthylurethane beyond 58 to 60°, whereas the derivative of the pure alcohol from peppermint oil melts at 72°. In spite of this discrepancy we do not hesitate to accept the identity of the alcohol with *β,γ*-hexenol. A closer examination carried out with more material will in all probability confirm this identity and thus prove the existence of free *β,γ*-hexenol in Spanish thyme oil.

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[1]) Cf. *Bericht* (German) 1921, 87. — [2]) *Estudio quimico de esencias naturales españolas.* Madrid 1919, p. 134. — [3]) *Report* 1918, 39; Walbaum, *Journ. f. prakt. Chem.* II. 96 (1918), 245.

In the next fractions we found after repeated, careful fractionation a *new terpene* with a carrot-like odour and the following constants: —

      1. B. p. 155°: $d_{15°}$ 0.8533, α_D +4° 50', $n_{D20°}$ 1.46201

      2. B. p. 155°: - $d_{15°}$ 0.8535, α_D +4° 58', $n_{D20°}$ 1.46221

      3. B. p. 155 to 156°: $d_{15°}$ 0,8537, α_D +4° 35', $n_{D20°}$ 1.46231.

The values obtained on combustion pointed to a terpene $C_{10}H_{16}$: —

      0.1822 g. substance gave 0.5879 g. CO_2, 0.1958 g. H_2O.

	- Found	Calc. for $C_{10}H_{16}$
C	87.98 per cent.	88.23 per cent.
H	11.93 per cent.	11.77 per cent.

      Mol. refr. found   calc. for $C_{10}H_{16}$
         43.89   43.51.

The nitrosochloride, purified by means of chloroform and methyl alcohol, shows a strong tendency to decompose and can therefore be prepared and purified only in small amounts. Decomposition starts at about 85° in a very sudden and violent manner. The piperidide melts at 194 to 195°, the nitrolbenzylamine indistinctly from 105 to 108°; the anilide was not obtainable, neither a solid nitrosate. When dissolved glacial acetic acid and cooled down the terpene adds somewhat more than two atoms of bromine; the resulting bromide remains oily. Likewise, the hydrochloride obtained by saturating, in glacial acetic acid solution, the terpene with hydrogen chloride gas was liquid. On trying to hydrate the terpene by action of acetic and sulphuric acids resinification resulted. When oxidized by means of permanganate solution, with cooling by ice (according to the method for obtaining pinonic acid), the terpene gave rise to a neutral oxidation product soluble in water and chloroform, which did not distil without decomposing and was therefore not yet obtainable in the crystalline state. On further oxidation with neutral permanganate at 100° there was obtained, in addition to oxalic acid, m. p. about 100°, and acetic acid (Ag estimated in the silver salt 64.20 per cent.), an acid which decomposed on distillation *in vacuo* and which evidently was not a ketonic acid. Treatment with dimethyl sulphate yielded no ester. Details as to the chemical structure of the terpene are to be expected only after closer investigation. We wish to add that this oil offered no clue for the presence of α-pinene, in contradiction to another oil which years ago[1]) we found to contain that terpene. Considering the great variety in the botanical origin of the Spanish thyme oils this different behaviour is by no means surprising.

A very small amount of *camphene* is present in the Spanish oil. It was identified by treating the fractions boiling above 157° in the usual manner with acetic-sulphuric acid, when a trifle of *iso*bornyl acetate (b. p. 82 to 88° at 6 mm.; sap. value 202) was isolated by fractionation. The free *iso*borneol obtained therefrom by saponification melted at 208 to 212°.

β-Pinene was likewise a constituent of the oil. After oxidising a fraction b. p. 165 to 169° with alkaline permanganate a hydrocarbon with the following constants was regenerated: — b. p. 163 to 167°, $d_{20°}$ 0.8520, α_D +3° 45', $n_{D20°}$ 1.46609, mol. refr. found 44.02, calc. 43.5. On further oxidation with permanganate is yielded nopinic acid, m. p. 126 to 127°. The hydrocarbon occurs in minute quantity only.

A hydrocarbon fraction, b. p. 165 to 168° ($d_{15°}$ 0.8567, α_D +3° 57', $n_{D20°}$ 1.47141) which on saturating with hydrogen chloride gas and after some standing had yielded

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[1]) *Report* October 1894, 57.

terpinene dihydrochloride, m. p. 52°, was suspected to contain sabinene. However, on oxidation with alkaline permanganate solution, no sabinenic acid was obtainable.

p-*Cymene* could be proved to be present only after many fruitless attempts, by oxidation of fractions b. p. 175 to 179° with strong permanganate solution, when α-hydroxy*iso*propylbenzoic acid, m. p. 153 to 154°, was the result. On boiling with strong hydrochloric acid the difficultly-soluble propenylbenzoic acid, m. p. 160 to 161°, was formed. The amount of cymene present is exceedingly small. As far back as 1856 Lallemand[1]) was able to prove the presence of p-cymene in a thyme oil. However, it must remain an open question whether in this case an oil of different botanical origin was under investigation or whether the p-cymene had been formed, by a secondary process, from terpinene, an important constituent of the oil.

γ-*Terpinene* is the main constituent of the phenol-free oil and could be traced in all sub-fractions b. p. 176 to 183°. All of these fractions gave on saturation with hydrogen chloride gas in glacial acetic acid solution, an oily hydrochloride which either was precipitated by addition of water or was obtained on evaporation of the solvent in an open dish after some standing, and could be brought to solidification by strong cooling and additionally after inoculation. When crystallized from methyl alcohol the dihydrochloride melted at 51 to 52°, and in mixture with the corresponding derivative of dipentene very considerable depression of the melting point was observed. From various of the afore-mentioned subfractions there was obtained, on oxidation with alkaline permanganate in the cold, the erythritol $C_{10}H_{20}O_4$ characteristic of γ-terpinene; m. p. 236 to 237°. On boiling with dilute sulphuric acid in a current of steam a smell of phenols (thymol, carvacrol) was noticed. When several fractions (b. p. 175 to 179°; 176 to 178°; 177°) were brominated in absolute ethereal solution, after being chilled down to freezing mixture temperature, separation of a solid, slightly yellow bromide was repeatedly observed which, however, on suction or on spreading on cooled porous plates decomposed rapidly with liquefaction and evolution of hydrogen bromide. Since just these fractions yielded γ-terpinene dihydrochloride in good amount it might have been the case of a bromide of γ-terpinene. Possibly the investigators working on terpinene have hitherto overlooked the fact that γ-terpinene, in absolute ethereal solution at reduced temperature forms a bromide which is unstable at ordinary temperature when exposed to the air. That α-terpinene was absent was concluded from the non-formation of the nitrosite; likewise we were unsuccessful in obtaining, by oxidation with alkaline permanganate, the dihydroxy dimethyladipic acid characteristic of α-terpinene which in many cases, besides γ-terpinene, is a constituent of essential oils.

Of *alcohols*, the following were found to be present: — *linalool, borneol, terpinenol-4,* and *geraniol.*

The first-named alcohol was found in fractions of the b. p. 77 to 78° (6 to 7 mm.) and the sp. gr. d_{150} 0.8975 to 0.8991 which were separated from fractions containing borneol by sharp fractionating. To judge from the odour, an oil of the b. p. 197 to 199.5° and the sp. gr. d_{150} 0.8750 consisted of fairly pure linalool from which the phenylurethane, m. p. 65°, was obtained without difficulty on treatment with phenyl-*iso*cyanate. Oxidation with bichromate mixture yielded citral.

l-Borneol separated off in the solid state from the fraction b. p. 86 to 102° (8 mm.) when distilling *in vacuo*, and was identified by its odour, its m. p. 204°, and by the formation of camphor on treatment with bichromate mixture.

[1]) *Jahresber. d. Chem.* 9 (1856), 616; acc. to *Annal. de Chim. Phys.* (3) 49 (1857), 148.

Fractions of the b. p. 86.5 to 91.5° and the sp. gr. 0.9403 and 0.9363 showed the characteristic smell of terpinenol reminding slightly of terpineol. Since they contained additionally a small amount of borneol which could not be removed by freezing-out the presence of terpinenol, an alcoholic connected structurally with terpinene and therefore often found in oils containing this terpene, had to be proved by oxidizing it, by means of cold 1 per cent. permanganate solution, to the glycerol $C_{10}H_{20}O_3$. The neutral product obtained hereby (b. p. 160 to 165° [9 mm.]) solidified soon when triturated with chloroform and ether. Whereas, however, Wallach[1] found the m. p. of the glycerol from terpinenol-4 to be 114 to 116° (glycerol from terpinenol-1, m. p. 120 to 121°), the glycerol obtained by us melted already below 100°, thus proving that the body was not uniform. Only after repeated fractional crystallization it was possible to isolate small amounts of the body with the m. p. 111 to 113°. When heated with dilute hydrochloric acid in a current of steam it yielded, in addition to cymene, carvenone; semicarbazone, m. p. 201 to 202°. The sublimate of the glycerol melted at 128 to 129°. A somewhat larger amount of the glycerol was prepared and transformed, by oxidation with alkaline potassium permanganate, into the a,a'-dihydroxy-a-methyl-a'-isopropyl adipic acids of the m. p. 205 to 206° and 188 to 189°. Although we did not succeed in separating the resulting mixture of the active and the inactive acid (m. p. 195 to 200°) into the separate acids with the correct melting point, it was possible to isolate, from the mixture of bilactones obtained by heating the acid mixture to 200° (m. p. 65 to 71°), the bilactone, m. p. 70 to 72°, corresponding to the acid m. p. 188 to 189°, by resorting to fractional crystallization. This bilactone easily passed over, on heating with caustic potash, into the acid m. p. 187 to 188°.

A further proof for the presence of *terpinenol*-4 in the fraction mentioned above was furnished by the formation of terpinene dihydrochloride, m. p. 51 to 52° when the solution in glacial acetic acid was saturated with hydrogen chloride gas. However, we were unsuccessful in attempting to prove the presence in the terpinenol-containing fraction of a-terpineol, which would account for the unsharp melting point of the glycerol $C_{10}H_{20}O_3$ owing to a possible admixture of the glycerol of a-terpineol (m. p. about 121°). It may, therefore, be taken for granted that the incorrect melting point of the neutral oxidation-product may be ascribed to the low content of borneol in the terpinenol fractions.

Small amounts of *geraniol* were found to be present in fractions boiling between 91.5 and 102° (7 mm.); $d_{15°}$ 0.9259; faint odour of geraniol. On treatment of the solution in benzene with phthalic anhydride and subsequent saponification of the resulting solution of the ester-salt, an oil, b. p. 225 to 231°, with a pronounced odour of geraniol was formed. It yielded a diphenylurethane, m. p. 82°; on oxidation with bichromate solution, citral was the result.

The high-boiling fractions (b. p. 102 to 106° [7 mm.]; $d_{15°}$ 0.9326 to 0.9386) were not entirely free from thymol. After the phenol had been removed and the liquid distilled over sodium, a sub-fraction showed the following properties: — b. p. 259 to 264°; $d_{15°}$ 0.9105; $a_D + 7°54'$. On heating with glacial acetic and sulphuric acids, followed by steam-distillation, caryophyllene alcohol, m. p. 94 to 95° was formed, so that the presence of *caryophyllene* in the sesquiterpene fraction was rendered probable. In addition, small amounts of a second sesquiterpene and possibly also of a sesqui-terpene alcohol seemed to be present in this Spanish oil.

Hence, the following bodies, besides thymol, have been proved to be important constituents of the oil in question: — a new terpene, b. p. 155°, camphene, γ-terpinene,

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[1] *Liebig's Annalen* 350 (1906), 169.

l-borneol, linalool, and terpinenol-4; amyl alcohol, amyl carbinols, β, γ-hexenol (?), β-pinene, p-cymene, geraniol, and caryophyllene are likewise present. Hitherto, the following constituents of Spanish thyme oil (however, of different botanical origin) had been found:—α-pinene, p-cymene, borneol, and linalool.

From the dry herb of *Thymus vulgaris*, L:, collected in July near Terracina, province of Rome, P. Leone and E. Angelescu[1] obtained by steam-distillation 1.06 per cent. of a dark red oil with a strong aromatic odour and the following constants:—$d_{40}^{18.50}$ 0.9250, α_{220} — 2.40° (taken in white electric light), n_{D220} 1.49646, a. v. 3.5, sap. v. 14.9; ester v. 11.4, corresponding to 4 per cent. linalyl acetate. Steam-distillation being repeated, the constants of the lemon-yellow oil were:—$d_{40}^{18.50}$ 0.9194, $[\alpha]_{D280}$ — 3.57°, n_{D280} 1.49505.

The phenol (*thymol*, m. p. of the nitroso derivative 141 to 142°) was removed by shaking with 5 per cent. caustic soda solution. Thymol estimated, 38 per cent., according to the iodine method of Kremers and Schreiner. The non-phenolic part of the oil showed, after acetylation, the sap. v. 112, corresponding to 30.8, and 14.1 per cent. when calculated on the entire oil. After repeated fractional distillation under ordinary pressure the following fractions were obtained:—1. up to 165° (1.3 per cent.); 2. 165 to 175° (23.1 per cent.); 3. 175 to 185° (30.8 per cent.); 4. 185 to 195° (6.5 per cent.); 5. 195 to 205° (5.5 per cent.); 6. 205 to 225° (4.8 per cent.); 7. 225 to 235° (10.6° per cent.). After boiling fractions 2 and 3 for five hours with sodium, the authors succeeded in obtaining 13 per cent. (calculated on the entire oil) of a fraction boiling at 171 to 176° which consisted nearly entirely of *cymene* (hydroxy*iso*propylbenzoic acid, m. p. 156 to 157°). The free alcohol seemed to be a mixture of borneol and linalool, which the authors, however, were unable to identify.

From a drug which in its morphological and anatomic characters coincided completely with *Thymus vulgaris*, L. R. Kofler[2] obtained an oil which differed largely from thyme oil owing to a content of *cineole* and containing but very little, if any, of thymol. The author takes this fact for a further proof for the extraordinary variability of the species of the genus *Thymus* also in their chemical behaviour[3]).

Turpentine Oil. — There are in the main three species of *Pinus* used in the United States for the production of turpentine; *viz., Pinus palustris*, Mill., which supplies the largest quantity by far, *Pinus heterophylla* (Ell.), Sudw., and *Pinus echinata*, Mill. The Bulletin No. 898 (1920) of the U. S. Dep. of Agriculture[4], which contains much useful information on the turpentine industry of country, names in addition to *Pinus palustris* and *Pinus caribœa (heterophylla)* also *Pinus ponderosa*, Dougl., (Western yellow pine)[5] as being tapped for turpentine. According to this bulletin, about 75 per cent. of the world's supply of turpentine is produced in the United States, the relative production in the various States being about as follows:— Florida, 37 per cent.; Georgia 19 per cent.; Louisiana, 15 per cent.; Alabama, 12 per cent.; Mississippi, 9 per cent.; Texas, 7 per cent.; North and South Carolina, less than 1 per cent. Formerly North Carolina produced the bulk of the world's supply of turpentine, but now its pine forests are almost exhausted.

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[1] *Gazz. chim. ital.* **51** (1921), II. 391. — [2] *Pharm. Monatsh.* **1921**, N° 3. Acc. to *Pharm. Ztg.* **66** (1921), 484. — [3] Dorronsoro found likewise in Spanish thyme oils originating from *Th. Mastichina*, L. and *Th. cephalotus*, L. up to 60 per cent. of cineole by the resorcinol method. Compare also p. 65 of the present *Report*. — [4] *Journ. Soc. chem. Ind.* **40** (1921), R. 165. — [5] Comp. also *Report* April 1913, 101. According to Engelmann, a botanist who died in St. Louis (Missouri) in 1884, *Pinus ponderosa* is the most widely spread pine of the West in California and Oregon, thriving on low and high mountains, even also in the plain, on sandy-gravelly soil. Beissner, *Handbuch der Nadelholzkunde*, 2nd edition, p. 387.

The distilling plant is simple and has not been improved materially during the last 50 to 60 years; it consits of a copper still of 500 to 1000 gallons capacity, with a still-head connected to a large copper condensing-coil cooled in water. From 7 to 14 barrels of oleo-resin go to make a charge, depending on the nature of the oleo-resin and the size of the still. This is heated over an open fire. When most of the water originally present in the oleo-resin has passed over, as shown by the peculiar sound which is heard close to the tail-pipe of the condenser coil, a small stream of water is admitted to the still. The yield of oil varies from 16 to 22 per cent. It is mostly shipped in wooden barrels, treated internally with two coats of glue and holding 50 to 53 gallons. In the more western States the larger producers employ tank-cars of 5 to 16 thousand gallons capacity. On arrival at the primary markets each barrel or tank-car is inspected as to quality and volume.

The total production in the U. S. A. for the 1919 season amounted to 366000 casks (50 galls.) of turpentine oil and 1237000 barrels (500 lbs.) of rosin; during 1920 up to August 1st, 237155 casks of turpentine oil and 712387 barrels of rosin were produced, the estimated production for the rest of the season being 233876 casks of turpentine oil and 739679 barrels of rosin.

At present a little less than 10 per cent. of the total is wood turpentine obtained from stumps and dead or fallen timber by steam or destructive distillation; this source of turpentine is becoming more important.

As per a statistics of the Turpentine and Rosin Producers' Association[1] the U. S. A. supplied before the war about 85 per cent. of the world's requirements of naval stores. At present, the percentage is only 62, the remaining 38 per cent. being contributed by France, Mexico, British India, Spain, Italy and other countries. Especially France has increased her production during the last four years. In 1920/21 it amounted to 250000 barrels (50 gals.) of turpentine oil and 875000 barrels of rosin. Spain supplied twice the quantity of previous years; viz., 41000 casks of turpentine oil. The exports of the U. S. A. in 1921 amounted to 73125 casks of oil and 508334 barrels of rosin (500 lbs.), as compared with an average of 359375 casks of oil and 1354068 barrels of rosin in the last ten years before 1914.

In Central and West Durango (Mexico), there are about 15000000 acres of pine forests, the larger part of which is owned be the Federal Government. As the material is fit for the production of turpentine, an American company erected there a modern distilling plant. The trees can be tapped for three to four years running. Each trunk yields during one season more than one quart of pure, white turpentine oil and 6 lbs. of rosin, the quality of which is not inferior to the products of other countries[2].

Spain's turpentine industry[3] is in the hands of the *Union Resinera Española,* one of the largest and most powerful trusts of the country. This company's report (1919) contains the following figures: —

Production	Rosin	Turpentine oil
1915	15054.593 tons	4331.429 tons
1916	16238.545 „	4868.871 „
1917	14364.773 „	4599.066 „
1918	13918.298 „	4101.384 „
1919	11397.619 „	3647.656 „

[1] *Drug and Chem. Markets* 10 (1922), 155. — [2] *Drug and Chem. Markets* 9 (1921), 1038. — [3] *Oil, Paint and Drug Reporter* 100 (1921), No. 21, p. 32.

Sales	Rosin	Turpentine oil
1915	15153.998 tons	4504.281 tons
1916	14273.563 „	5670.763 „
1917	17269.470 „	4414.491 „
1918	9321.734 „	4198.808 „
1919 . . : . .	14257.651 „	4408.147 „

Spain's exports of turpentine oil, rosin and tar were as follows:—

	1919	1920	in first 4 months 1921
Terpentine oil . .	4591.216 tons	3081.873 tons	518.495 tons
Tar . . . : . . .	13041.131 „	12181.345 „	1039.588 „
Rosin	809.243 „	544.484 „	36.159 „

Portugal produced[1]:—

Year	Rosin	Turpentine oil
1916/17	3000 tons	950 tons
1917/18	4000 „	4200 (?) „
1918/19	6000 „	2000 „
1919/20	6300 „	1800 „
1920/21	12400 „	3600 „

It is reported that there are no stocks of turpentine oil, whereas those of rosin are estimated at about 10000 tons. Portugal's home consumption is 2000 tons each of turpentine oil and rosin, annually. The pine forests of Portugal (773000 hectares) cover about the same area as those of south-western France (200000 hectares in the Gironde, 500000 hectares in the Landes and 50000 hectares in the Lot-et-Garonne).

According to Th. M. Ainscough[2] the Indian production of rosin and oil of turpentine becomes more and more important. It started on a small scale about 25 years ago and, owing to the activity and the skill of the foresters, who were well acquainted with the methods employed in the "Landes" of France (gemmage à vie and gemmage à mort)[3] developed first in the United Provinces of India and later on in the Panjab to its present state. In 1919 an area of 97525 acres of pine forest (in the main Pinus longifolia, Roxb.) yielded 4615 tons of oleo-resin, from which 2400 tons of rosin and more than 156000 gallons of turpentine oil were prepared[4].

F. Henrich[5] reports on an investigation of pine balsams (Pinus silvestris, L.), carried out conjointly with A. Pfotenhauer and under the assistance of F. Pensel. Generally speaking the samples, which came from the neighbourhood of Erlangen and had been collected in different months of 1917 and 1918, had the same composition:— $d_{40}^{20°}$ 0.8560, 0.8573, $[\alpha]_{D20°}$ + 16.1, + 13.6°; acid v. 0.61, 0.40; ester v. 1.67, 1.58; sap. v. 1.73, 1.62[6]. The resinous residue of one balsam, collected in August from trees growing on fatter soil, contained even less esters than that of the other balsams. About 22 to 25 per cent. of the balsam were volatile with steam[7]. The turpentine oil whose angle of rotation did not exceed $[\alpha]$ + 28.41°, consisted of a small quantity of β-pinene (nopinic acid,

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[1] Oil, Paint and Drug Reporter 100 (1921), No. 21, p. 32. — [2] Ibidem 101 (1922), No. 1, p. 32. — [3] Comp. Gildemeister and Hoffmann, The Volatile Oils, 2nd edition, vol. II, p. 69. — [4] Comp. also Berichte (German) 1920, 132; 1921, 48. — [5] Zeitschr. f. angew. Chem. 34 (1921), 363. — [6] There seems to be a printer's error, for the sum of the acid and ester values must equal the saponification value. — [7] Comp. Report 1916, 54.

m. p. 126°) and apparently a mixture of d- and l-α-pinene, in which the d-α-compound predominated (nitrosochloride 103°).

The authors found too that the unsaponified fraction of the crude oil of turpentine had a somewhat higher specific gravity than the saponified fractions, but that the optical rotation was not considerably influenced by the saponification. It was impossible to establish what the components of the saponified products were.

One sample of turpentine oil (d_{40}^{20} 0.8624; $[\alpha]_{D20} + 17{,}13°$, C = 87.0 per cent.; H = 11.12 per cent.) was exposed to the air and examined from month to month. After six months the constants were:—d_{40}^{20} 1.0584, $[\alpha]_{D20} + 1.44°$, C = 71.03 per cent., H = 9.45 per cent. In another sample of purified turpentine oil from pine balsam, which had been kept for three years in an Erlenmeyer flask, the presence of small quantities of a peroxide, of acid-like components (not abietinic acid) and of 20 per cent. of resene was proved. (Tschirch found in a six months old, autoxidized French turpentine oil above all a resene-like body in addition to a small amount of resinolic acid. *Arch. d. Pharm.* 238 (1900), 645.) Besides, the authors obtained from this sample a small quantity of a dextrorotatory oil, smelling like menthol, but which it was impossible to examine any further.

M. Vèzes[1]) thinks it possible to determine the proportion of α-pinene and β-pinene (nopinene) in French turpentine oil with the aid of Darmois'[2]) polarimetric method. The proceeding, which it would lead us too far to describe in detail, consists in that the rotatory power of 5 fractions of equal size is determined for three colours. With the aid of the known rotatory power of α- and β-pinene the proportion of the quantities of these terpenes can easily be calculated. Vèzes found in this way that a French oil of turpentine (b. p. 154 to 162° under ordinary pressure, without the less volatile hydrocarbons) contained 80.9 per cent. of α-pinene. It may be added that the author himself thinks the method has not been sufficiently verified yet and that he calls the values found only approximately correct.

F. C. Palazzo, Mina Palazzo and E. Azzarello have published conjointly a series of articles[3]) on investigations of Italian turpentine oil, the results of which have been discussed in part in our previous *Reports*[4]) (on oil of turpentine of *Pinus Pinea*, L., and of *Pinus Pinaster*, Sol.).

One of these articles (no. III by F. C. Palazzo and E. Azzarello) deals with the applicability of Italian oil of turpentine. As has been shown before, the oil obtained in Tuscany[5]) (b. p. 170 to 172°, d_{150} 0.852, n_{D20} 1.474, inflammation point 50°) consists chiefly of l-limonene and differs considerably from the products of other countries, which contain α-pinene above all. It is pointed out in the article, why just these properties (lesser volatility, better capacity for dissolving resins, balsams, fats and waxes, elevated inflammation point, &c.) make the Italian turpentine oils very fit and valuable for certain technical purposes, such as the manufacture of varnishes, oil paints, &c. It is further mentioned that the vapours of these oils, contrary to the products containing pinene, do not injure the human organism.

Pinus halepensis, Mill., the turpentine of which might likewise be put to use, also occurs in Italy. M. Palazzo[3]) investigated oils of turpentine, obtained from *Pinus halepensis* in Cecina and Vada. The yield in turpentine which was obtained according

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[1]) *Compt. rend.* 172 (1921), 977. — [2]) *Thèse*, Paris 1911, p. 53. — [3]) *Le trementine italiane.* Nota I, II, III, IV. From *Annali del R. Istituto Superiore Forestale Nazionale*, vol. II, 1917 and vol. IV, 1919. As per a reprint kindly sent us. — [4]) Comp. *Report* 1917, 72; 1918, 50. — [5]) The turpentine of the different *Pinus* species, among which *Pinus Pinea* preponderates, are not distilled separately.

to the method used in the Landes[1] in the course of about five months, was approximately 1.3 kilos per tree. If the normal time of seven to eight months was allowed, Palazzo thinks that the output could be increased to 1.8 kilos per tree.

The product yielded on an average about 20 per cent. of turpentine oil with the following properties: — d_{150} 0.8635, $[\alpha]_{D150}$ + 46.71°, n_{D150} 1.4688, soluble in 7 parts of 90 per cent. alcohol, inflammation point 32 to 33°. When subjected to fractionated distillation, the six first fractions (90.4 per cent.) passed over between 154 and 158° and consisted almost exclusively of d-pinene. The 7th and 8th fractions boiled from 158 to 160° and from 160 to 163°, respectively.

The methods for detecting and estimating toluene, xylene, solvent naphtha and other coal-tar derivatives in turpentine oil, as suggested by Marcusson[2] and Krieger[3] have not been found reliable by V. E. Grotlisch and W. C. Smith[4] especially if small quantities are concerned. Grotlisch and Smith have therefore contrived a new method, according to which the turpentine oil is first treated with dry hydrogen chloride. The pinene hydrochloride formed is separated from the other liquid, which is then distilled under reduced pressure The unchanged coal-tar oils pass over with the first part of the distillate. This is sulfonated with fuming sulphuric acid and distilled with steam. In the case of pure oil of turpentine, a very small quantity of a dark yellow volatile oil of disagreeable smell is obtained: — index of refraction n_{D20} slightly above 1.500. If any mineral oil is present, an almost colourless product is obtained, having the characteristic mineral oil odour and an index of refraction below 1.500, generally below 1.4800. If coal-tar derivatives were present, they can be recovered as such to the extent of 45 per cent. The quantity present thereof is found therefore by multiplying the result of the analysis with 2.2. — The sulphuric acid used must always have the same concentration and contain 3 to 4 per cent. of free SO_3. Otherwise the results do not agree. This method is not strictly applicable to wood turpentine oil, unless the adulteration exceeds 4 per cent., as small quantities of benzene hydrocarbons occur as normal components of this oil.

With reference to Salvaterra's article "On New Methods of Investigating Turpentine Oil", in which the author declares that Herzfeld and Marcusson's method is not altogether free from objection[5], J. Marcusson[6] points out once more the usefulness of his nitric acid test for the determination of light petroleum in turpentine oil. According to these explanations Marcusson's investigations of mixtures of light petroleum and turpentine oil would prove that his method suffices completely for technical purposes. The nitric acid method is applicable not only for turpentine oils, but also for pine oil and pinolene and does not depend upon what sort of light petroleum is present. Even small quantities, such as 2 to 3 per cent. of light petroleum, were still to be detected with his method.

H. Heller[7] publishes an extract of H. Salvaterra's article on the investigation of turpentine oils[8] discussed by us already, under the title of "New Methods for the Investigation of Turpentine Oils".

As C. M. Sherwood[9] reports, the extraction of rosin, pine oil and turpentine from dead pine wood was begun in 1909 by the Yaryan Naval Stores Co. at Gulfport and Brunswick, Ga., Since 1921 this company works conjointly with the Hercules

[1] *Gemmage à vie* or *gemmage à mort;* comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 69. — [2] *Chem. Ztg.* 36 (1912), 431. — [3] *Ibid.* 40 (1916), 972. — [4] *Journ. Ind. and Eng. Chem.* 13 (1921), 792. — [5] Cf. *Bericht* (German) 1921, 49. — [6] *Chem. Ztg.* 45 (1921), 418. — [7] *Deutsche Parf.-Ztg.* 7 (1921), 131. — [8] Cf. *Bericht* (German) 1921, 48. — [9] *Chem. and Met. Engin.* 25 (1921), 994.

Powder Co.[1]) The combined maximum worked per day is about 1000 tons of wood. As Sherwood declares, it cannot be said that this industry has been profitable up to the present time, but it may nevertheless be called upon to act an important part in future in the production of naval stores. The wood chiefly used is the Southern long-leaf pine. *(Pinus palustris)*. The material may be divided in stump wood and top wood, the former being richer in extractable products. It seems to be generally true that the twisted grain wood is richer than the straight grain. The distribution in the roots is also interesting. The lateral roots are very rich in rosin, turpentine and pine oil; the tap root is soft and spongy and contains practically no valuable products. Good land yields 8 to 15 tons of wood per acre, depending on the section of the country. The milled wood is steamed for 3 to 4 hours in an extractor, when all the easily boiling constituents (called turpentine by the author) and about half of the less volatile ones (pine oil) are distilled off. This distillate, consisting of approximately 70 per cent. of light and 30 per cent. of heavy wood turpentine oil is then fractionated. The steamed wood is boiled with a solvent, generally gasoline, in order to obtain the rosin and the heavy oil still left behind. The solvent and the heavy oil extracted are separated from the rosin by repeated distillation.

The light wood turpentine oil obtained that way distinguishes itself by its uniformity and has the following constants: — initial b. p. 154°, constituents boiling below 170° = 90.5 per cent., residue 1 per cent., $d_{15.5°}^{15.5°}$ 0.865, $n_{D15.5°}$ 1.469, flash point (Abel, closed cup) 34°. This wood turpentine oil has not the fragrant, sweet odour of freshly distilled gum turpentine oil.

A high-grade commercial pine oil manufactured at Brunswick, Ga., had the following properties: — boiling range 180 to 225°, $d_{15.5°}$ 0.935, $n_{D15.5°}$ 1.479, residue 3 per cent., colour light straw. According to Sherwood, the composition of pine oil, which resembles turpentine oil very closely, is rather uncertain. We would mention therefore that, years ago[2]) we thoroughly investigated a yellow pine oil, *i. e.*, a wood turpentine oil obtained from the stumps, most likely from *Pinus palustris,* and found the following constituents: *l*-α-terpineol, α- and β-pinene, camphene, *l*-limonene, dipentene, γ-terpinene, cineole, *i*-fenchylalcohol, campher, *l*-borneol and methylchavicol.

Pine oil when first produced was considered practically worthless. In later years, however, it has become valuable in many ways, *e. g.* in the flotation process, as basis of a variety of medicinal and desinfectant solutions and as a solvent in the rubber, paint and varnish industries.

The rosin obtained through the extraction is generally ruby red and consists, like ordinary rosin, chiefly of abietic acid, $C_{20}H_{30}O_2$[3]). The percentage found by analysis were C 78.12, H 9.90 and O 11.98 per cent. Wood rosin is said to have an advantage over gum rosin because of its uniformity and cleanliness.

Also in Germany stumps are used again on a larger scale for the production of turpentine oil. As F. O. Koch[4]) reports, the following yields were obtained from resinous stumps (root wood of *Pinus silvestris,* L.) according to Franz Schmidt's method: 5 per cent. oil of turpentine, 1 per cent. acetone, 8 per cent. tar and 22 per cent. charcoal. Koch then makes some remarks concerning the problem of the production of turpentine and pine oils from stump wood, remarks which are not altogether reliable and invite

[1]) In 1910 there were 30 plants in the U. S. A., where yellow pine was distilled, in addition to smaller quantities of Norway pine and Douglas fir. Cf. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd edition, vol. II, p. 98. — [2]) *Report* April 1910, 103. — [3]) The acid $C_{20}H_{30}O_2$ is pimaric acid. — [4]) *Chem. Ztg.* 45 (1921), 699.

criticism. Link[1]) has already found the proper answer, so that we may refrain from going into details. We would only add that the good quality of the French product is due to the peculiar composition of the French turpentine, and to the methods of producing the gum and distilling the oil. Koch's assertion "that an excess of volatile constituents in the gum, the loss of which during the exudation has no great effect" was responsible for the superiority of the French turpentine oil, is absolutely unfounded. As to the author's opinion that the direct production of turpentine oil from stumps had so far been unknown in Germany and other countries, Link remarks that about 40 years ago already an excellent pure turpentine oil has been obtained by steaming resinous wood. Link mentions that he himself constructed a factory in Western Prussia, in 1893, and another in Volhynia, in 1901, where the oil was drawn from the wood in a specially constructed apparatus, before being carbonized. The high costs of production, combined with the competition from abroad, which sent the prices down, prevented the construction of more such plants. He thinks that now conditions have altered somewhat, as more trees are cut in the forests and the competition of other countries is less keenly felt.

The factory in Volhynia, erected by Link, produced in the first four years 1554 tons of turpentine oil, 144.48 tons of pine oil, 10298.4 tons of tar, 1680 tons of acetate of lime (80 to 82 per cent.), 210 tons of wood-spirit (calculated as 100 per cent.) and 12196.8 tons of charcoal, from 168000 cubic metres of wood.

The products offered as turpentine oil in Esthonia during the last three years were, according to J. Schindelmeiser[2]), exclusively pine or sulphate oils. The pine oil produced in Esthonia contained from 50 to 75 per cent. of pinene; that from the East was also rich in pinene, whereas the Finnish product contained more cymene. If, like in Finland, the oil is obtained at a higher temperature, cymene forms at the expense of the pinene. The Esthonian crude oil differed greatly in that sometimes up to 75 per cent. could be distilled off with steam, but in some cases barely 20 per cent. The sulphate oil, coming from the Swedish wood pulp factories, but bought and sold as French oil, consisted almost entirely of cymene.

The odour of sulphate turpentine oil can be improved according to L. Schmidt[3]) by heating the oil for two hours with sodium peroxide under a reflux condenser. The product is then filtered in order to separate it from the yellow deposit formed and distilled with steam. The turpentine oil thus obtained is said to resemble the French oil.

F. Baum, of Jena University's Women's Hospital, used against certain inflammations injections of the following kind: turpentine oil 4 grams, eucupin 0.2 grams, olive oil 16 grams. As albuminuria was sometimes noticed after this treatment, one must be careful in case of inflammation of the kidneys[4]).

As a treatment of spotted fever, A. Brenner[5]) recommends oil of turpentine (to be taken every hour in doses of 0.05 to 0.1 gram) or terpin hydrate. Besides, the remedy is to be inhaled.

Valerian Oil. — In Belgium, the costs of the production of valerian root, including farmt-rent, wages, &c., are four times as high as before the war. The 1920 crop is said to be of very good quality, the roots being clean, heavy, of light colour and

¹) *Chem. Ztg.* 45 (1921), 820. — ²) *Pharmacia* 1921, No. 3, p. 16. — ³) D. R. P. 340126, dated 27. II. 1919. As per *Chem. Zentralbl.* 1921, IV. 1016. — ⁴) *Med. Klinik* 1921, No. 13. As per *Vierteljahresschr. f. prakt. Pharm.* 18 (1921), 130. — ⁵) *Münch. med. Wochenschr.* 1921, p. 992. As per *Therap. Halbmonatsh.* 35 (1921), 642.

likely to keep in good condition for several years. As the cultivation of valerian is no longer profitable enough, the Belgian farmers mean to continue it only, if better prices can be obtained[1]).

Indian Valerian Oil. — Valerian root from the western spurs of the Himalayas contains an essential oil, of which a sample was sent us recently. It behaved as follows: — d_{15° 0.9361, α_D —34° 6′, n_{D20° 1.48712, acid v. 37.3, ester v. 39.8, ester v. after acetylation 69.1, soluble in 0.3 vols. and more of 90 per cent. alcohol, whereas of 80 per cent. alcohol even 10 vols. did not suffice for dissolving the oil. The colour was yellowish green, the odour strong and lasting.

We were told that it came from *Valeriana Wallichii*, DC.

Vetiver Oil. — We stated quite a new kind of adulteration in a Réunion distillate, received some time ago. Among other substances, it contained glycerin acetate, an admixture which we had not expected at first. The oil was conspicuous by its properties: — d_{15° 0.9911, α_D +6° 20′, n_{D20° 1.51862, acid v. 0.5, ester v. 43.5, not yet soluble in 10 vols. of 80 per cent. alcohol. Comparing these figures with those for normal Réunion vetiver oils (d_{15° 0.990 to 1.020; α_D +22 to +37°; n_{D20° 1.515 to 1.527; acid v. 4.5 to 17; ester v. 5 to 20; soluble in 1 to 2 vols. of 80 per cent. alcohol), one sees at once that oil deviates the polarized light far too little, has too low an acid value and too high an ester number, whereas the solubility is absolutely insufficient. As these properties do not tally either with those of vetiver oils from other sources (Fiji Islands, Seychelles), there was sufficient cause for suspecting adulteration. Although we could not say anything definite straight off, we had to refuse the oil. The supplier, most likely in France (we bought the article from a middleman) was very indignant in consequence, but soon assumed a different tone, when we let him know that we had meanwhile succeeded in proving the presence of glycerin acetate in the oil. The following observation had shown us the way. The part of the oil which was insoluble in 80 per cent. alcohol and the soluble part, after having been separated off on adding water to the solution, were both lighter than the original oil. It was therefore evident that the alcohol had also taken up a heavier component which, as water did not separate it off, had to be soluble in water. It was therefore natural to think of glycerin acetate, the presence of which could be proved on closer investigation. It was recognized by its specific gravity (d_{15° 1.1654) and the high saponification value (671.6). The quantity was 5 per cent.

No doubt there was still another adulterant present, for the exceedingly low rotatory power and the insufficient solubility are not fully explained by the above remarks. Cedarwood oil probably had something to do with it, but we had no cause for further investigation, as the oil was taken back.

Oil of the roots of Viola odorata. — One of the oils formed by the decomposition of a glucoside is, according to A. Goris and Ch. Vischniac[2]), the oil contained in the roots of the sweet violet, which was discovered quite by chance. At a place where violets (*Viola odorata*, L.) grew abundantly, the authors noticed quite a strong violet smell, although the plants had no flowers as yet. On closer investigation, it resulted that the somewhat herbaceous and impure violet odour emanated from the fresh roots, when rubbed. Fowl had scratched there, had thus laid the roots bare and damaged them, which caused them to smell. In order to study the matter further, the authors

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[1]) *Chemist and Druggist* 94 (1921), 404. — [2]) *Bull. Roure-Bertrand Fils*, April 1921, 3.

sterilized 122 kilos of roots, collected near Grasse in March, and extracted them thoroughly with hot alcohol, to which some calcium carbonate had been added. The product was extracted with hot, aqueous acetic ester and the resulting green extract treated with hot water. The watery solution contained the glucoside and part of the already free oil, which was separated with the aid of ether. When some powdered violet root, which had previously been washed with alcohol and ether, was added to the aqueous liquid, a slight alteration of the rotation and the presence of a small amount of essential oil was to be noticed[1]).

Only a very few data are given about the oil itself. The yellow, aromatic product was partly soluble in light petroleum. This component proved to be a cristalline mass, which, after having been dissolved in an aqueous solution of sodium carbonate, could be precipitated with hydrochloric acid. On treatment with ether, a cristalline mass was then obtained which gave a green colour reaction with ferric chloride solution.

From the part that did not dissolve in light petroleum, a small quantity of salicylic acid was obtained after saponification with alcoholic potash lye. The authors take it that methyl salicylate was probably present in the roots, as Desmoulière[2]) arrived at the same result, years ago, with *Viola tricolor.*

Oil of Vitex trifolia. — On distilling the leaves and twigs of *Vitex trifolia,* L. (*Vitex ovata,* Mak. [?] [Thunb.]), a verbenacea grown in the Ogasawara Islands and Kanagawa Prefecture (Jap. *hámago*), Y. Shinosaki[3]) obtained 0.11 to 0.28 per cent. of an oil having a brown colour and a characteristic odour[4]). Three samples of the oil had the following characters: — d_{15^0} 0.8908 to 0.9141; α_{D20^0} — 39° 6' to — 47° 20'; n_{D20^0} 1.4707 to 1.5010; acid v. 0 to 1.75; sap. v. 23.38 to 38.70; sap. v. after acet. 40.14 to 53.34. The chief constituents of the oil were l,α-pinene, which gave no solid nitrosochloride, camphene (together with pinene: — 55 per cent.), terpinyl acetate (10 per cent., b. p. 84 to 86° at 15 mm.; d_{15^0} 0.9629; n_{D20^0} 1.4670); a diterpene alcohol $C_{20}H_{32}O$ or $C_{20}H_{34}O$ (20 per cent., b. p. 165 to 167° at 4 mm.; d_{15^0} 0.9760; α_{D20^0} — 46° 39'; n_{D20^0} 1.5143; sap. v. after acet. 42.02). The oil was separated into its three chief constituents by fractional distillation; the middle part might be suitable for perfumery purposes, as it is mainly composed of terpinyl acetate.

Oil of Water-hemlock. — A trial distillation of faded roots of water-hemlock (*Cicuta virosa,* L.) gave us an opportunity of determining some properties of this oil, which is but little known. It was yellow and had a faint odour, which it is difficult to describe. A similarity with water-fennel and celery, noticed by others on a previous occasion[5]), could not be stated this time. The following constants were determined: — d_{15^0} 0.8909, α_D + 16° 32', n_{D20^0} 1.48480, acid v. 3.7, ester v. 17.7, soluble in about 4 volumes of 90 per cent. alcohol, but with turbidity which, on standing, led to the separation of flakes (paraffin?). The yield amounted to 0.04 per cent.

Wormwood Oil. — F. Rabak[6]) publishes the following observations wade with wormwood, *Artemisia absinthium,* L., under cultivation at the Arlington Experimental Farm, Arlington, Virginia, for a period of years. During that time the plant was

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[1]) These facts indicate the presence of a glucoside, it is true, but the authors themselves have to admit that it has not been proved as yet. — [2]) Cf. *Report* April 1904, 88. — [3]) *Journ. chem. Ind., Japan* 24 (1921), 191. *Journ. Soc. chem. Ind.* 40 (1921), A. 411. — [4]) Years ago, a sample of the essential oil of *Vitex trifolia,* L. has been distilled from a specimen growing in the Botanical Garden of Sumatra, which contained cineole. Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. III, p. 409. — [5]) Cf. Gildemeister and Hoffmann *The Volatile Oils,* 2nd edition, vol. III, p. 326. — [6]) *Journ. industr. and engin. Chem.* 18 (1921), 536.

distilled both in the fresh flowering and in the dry condition, and also at different stages of growth. A number of the oils obtained were subsequently examined in the laboratory and compared from the standpoint of their physical and chemical properties. The conditions of distillation in every instance were identical. The yields of oil from the fresh flowering herb varied with the climatic conditions from year to year, oscillating in the period from 1907 to 1919 between 0.12 and 0.24 per cent. The greater the number of clear and partly cloudy days, the greater was the tendency of the plant to high yields of oil, whereas high rainfall and low temperature apparently tended toward low content of oil. The oils distilled from the dry plants were uniformly darker in colour and stronger in odour. They had a higher ester content (thujyl acetate 35 and 27.3 per cent.) than the ordinary oil (thujyl acetate 32.2 and 24.1 per cent.). It seems therefore that drying favours the formation of ester[1]). The maximum yield of oil was attained during the budding and flowering period. There was a decided decrease in the fruiting stage of the plant (in 1910: — from 0.20 to 0.08 per cent.). The content of free acids (as acetic) and of thujyl alcohol decreased as the plant passed from the budding to the fruiting stage.

Wintergreen Oil. — We would briefly mention two wintergreen oils received from Java (doubtless from *Gaultheria punctata*, Blume), as such distillates are found in commerce from time to time. They were colourless and behaved, as regards odour and constants, very much like the Indian oil of the same botanical origin, described by us some time ago[2]): — d_{15^o} 1.1873 and 1.1861, $\alpha_D \pm 0^o$, n_{D20^o} 1.53639, acid v. 5.4 and 4.8, ester v. 364.9 (= 99 per cent. of methyl salicylate) and 356.6 (= 96.8 per cent. of methyl salicylate), soluble in 7 and 8 volumes, respectively, or more of 70 per cent. alcohol.

These oils differ from the American distillate of *Gaultheria procumbens*, L., in that they are optically inactive; besides, their aroma is not so fine.

Indian Wintergreen oil. — According to Puran Singh[3]), the fresh leaves of *Gaultheria fragrantissima*, Wall., collected in Assam during the winter, gave as much as 0.65 per cent. of oil, or 1.2 per cent. calculated on dry material. The Nilgiri plant gave only 0.12 per cent. of oil from fresh leaves. The plant grows gregariously in the Nilgiris, in Assam and Ceylon, but for a regular supply of the leaves it would be necessary to cultivate it on an extensive scale.

Wormseed Oil. — The demand seems to increase in the Dutch Indies too. As the Dutch Chamber of Commerce in New York[4]) communicates, considerably larger quantities of wormseed oil were produced in 1920, mostly in plantations connected with the cultivations of the Government. Nevertheless the home production was not large enough to satisfy the demand.

As so much attention has recently been paid to the East Indian wormseed oil[5]), a sample originating from Java was very welcome, as it gave us an opportunity of getting acquainted with that product. The following constants were observed, d_{15^o} 0.9662, $\alpha_D + 0^o 4'$, n_{D20^o} 1.47867, acid v. 0.9, ester v. 9.8, soluble in 5.8 vols, and more of 70 per cent. alcohol, there being a slight turbidity in the beginning. The odour differed somewhat from that of the American oil, the smell of ascaridole being less strong.

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[1]) It must be taken into consideration, however, that the volatile constituents escape during the drying process. — [2]) *Report* October 1911, 97. — [3]) *Perfum. Record* 12 (1921), 51. — [4]) *Holland and her Colonies* 1 (1921), No. 7, page 15. — [5]) Comp. *Berichte* (German) 1920, 59; 1921, 15.

Our friends say that in Java only the seeds are distilled. The oil obtained in a comparatively small quantity is not exported but consumed in the country. It is considered inferior to the American product, as it is said to contain less ascaridole. The wormwood cultivation in Java is rather difficult, as the seeds do not ripen at the same time. The plant itself remains low and herbaceous. Plantations on a large scale have been abandoned, as it was recognized that it would be impossible to compete with the United States under normal conditions.

Chenopodium herb *Oil.* — As is known, the American wormseed oil is distilled from the seeding plant of *Chenopodium ambrosioides*, L., var. *anthelminticum*, Gray. We had an opportunity of late to distil the herb by itself and shall here report on our experience.

Fresh chenopodium herb, without seeds, yielded 0.0057 per cent. of an olive-green oil showing the following constants, d_{15^o} 0.8552, $\alpha_D + 1^o$, n_{D20^o} 1.48141, acid v. 2.7, ester v. 28.9, soluble in 5 vols. and more of 90 per cent. alcohol with slight opalescence.

From a second sample of herb, just beginning to seed, 0.034 per cent. of a brown oil were obtained, which had a higher specific gravity and a higher index of refraction and dissolved a little better than the one before mentioned: d_{15^o} 0.8795, $\alpha_D + 1^o 15'$, n_{D20^o} 1.48403, soluble in 1.4 vols. and more of 90 per cent. alcohol.

The extremely feeble odour was remarkable with both oils. They lacked almost completely the typical smell of ascaridole, so that it is to be supposed that they contained very little of this essential constituent. This would account perhaps for the low specific gravity and the insufficient solubility. It is remarkable too that the oils were dextrorotatory.

We are unable so far to explain these abnormalities. It is questionable whether they are only due to the absence of seeds, or whether the fact that the herb was grown in Germany, under conditions of climate and soil differing from those in America, is responsible for them.

Since some confusion exists as to the question to which constituent of the oil the anthelmintic action is due, Th. A. Henry and H. Paget[1]) undertook a re-examination of the oil. Six samples of commercial oils were used, with the constants: — $d_{15^o}^{15^o}$ 0.9582 to 0.9723, $[\alpha]_{D15^o}$ — 4.5 to — 6.8^o. The oils were separated by distillation under 15 mm. pressure into three fractions: — 1) b. p. below 84° (25 per cent.), 2) 84 to 104° (15 per cent.), 3) 104 to 118° (55 per cent.), the residue (5 per cent.) being chiefly ascaridole glycol. The first fraction consisted mainly of hydrocarbons, furthermore butyric acid (Ag-salt), methyl salicylate (below 5 per cent.; m. p. of the salicylic acid 156°; benzoate of the ester, m. p. 83°). The hydrocarbons were α-terpinene (nitrosite, m. p. 155°), a new lævorotatory terpene (with the approximate constants: b. p. 177 to 178° [760 mm.], d_{15^o} 0.847, $[\alpha]_{D15^o}$ — 57°, n_{D20^o} 1.484; tetrabromide, m. p. 117°, inactive) and p-cymene. The second fraction contained hydrocarbons and ascaridole, the third consisted of nearly pure ascaridole (b. p. 108 to 110° [15 mm.], d_{15^o} 1.0120, $[\alpha]_{D15^o}$ — 0.5^o).

According to the statements of the authors, sylvestrene, limonene, phellandrene, safrole and camphor were absent. The new terpene, which could not be separated from α-terpinene and p-cymene, yielded on oxidation with potassium permanganate acetic acid, *iso*butyric acid and a minute amount of a volatile acid, m. p. 117°, crystallising in long, slender needles, but insufficient for examination. On oxidising α-terpinene with potassium permanganate in acetone solution, the authors obtained two optically inactive forms of α,α^1-dihydroxy-α-methyl-α^1-*iso*propyladipic acid (m. p. 203

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[1]) *Journ. chem. Soc.* 119 (1921), 1714. From a copy kindly furnished by the authors.

to 204° and 189°), which Wallach[1]) had obtained formerly when oxidising terpinen-4-ol
from marjoram oil. Wallach's acid of the m. p. 205 to 206° was, however, optically active.

From two samples of Indian chenopodium, *Ch. ambrosioides* and *Ch. anthelminticum,* the
authors distilled 0.17 and 0.24 per cent. oil having the constants $d_{15°}^{15°}$ 0.9399, $[\alpha]_{D15°}$ +0.07°
and $d_{15°}^{15°}$ 0.9080, $[\alpha]_{D15°}$ — 9.6° respectively.

We extract the following from P. van der Wielen's[2]) treatise on chenopodium
oils: — According to the publications of Schüffner and Vervoort[3]) American wormseed
oil quickly gained a world-wide fame as a remedy against the widely-spread hook-worm
disease, owing to the support of the Rockefeller Institute. Said complaint is caused
by two intestinal worms, namely *Ankylostoma duodenale,* found in the mines not only
north of the Alps, in·France, Germany, Austria, Hungary, Belgium and England, but
also in subtropical and tropical climates, and the perhaps still more dangerous *Necator
americanus,* occurring in the South of North America, in Puerto Rico, Cuba and Brazil.
The disease may be brought about by drinking impure water, containing larvæ of the
worms, or by infection through the skin. In places where the skin is thin, as for
instance on the ankles, the larvæ penetrate into the body, pass through the blood-
vessels, the lungs, the larynx and the esophagus into the digestive system and there
develop. The miners generally get the disease in this way.

However successful a remedy chenopodium oil may be, its noxious qualities
ought not tn be underrated, for it may quite unexpectedly give rise to cases of
poisoning. In the report of the Rockefeller Institute of February 1921, Darling and
Smillie mention three such cases, caused by a chenopodium oil that had produced
no ill effect with other patients. The maximum dose for grown-up people ought to
be fixed at 3 cc. of the oil. On the other hand, the efficacity is said to have some-
times been less than expected, of proof that the anthelmintic properties of the com-
mercial oils, the constants of which were not always the same, could be very
different[4]).

L. Sullivan[5]) has made a detailed investigation into the manufacture of oil of
wormseed in Carroll County, Maryland. The belt in which the wormseed *(Chenopodium
ambrosioides)* is grown, he says, extends from a short distance north of Weston almost
due south to Woodbine, being about 15 miles long and approximately 4 miles wide.
The plant grown outside this belt is said to be far less productive of oil, and the
product is not so good. There are several hundred farms on which the herb is culti-
vated systematically and gathered, the crop being taken to distilleries, of which there
are about a dozen in the county. The largest individual farm does not exceed 13 acres,
and the biggest company-owned plantation is about 20 acres. The annual production
varies from 10000 to 40000 lbs., whereas it was only 2800 lbs. in 1910 and 5000 lbs.
in 1911. The 1920 yield is stated to have been relatively small, but the acreage culti-
vated was larger than usual. The better the soil is worked and manured, the higher
the percentage of oil in the plant. The yield in oil may run from 30 to 100 lbs. per acre.

According to Chevalier[6]) *Chenopodium ambrosioides,* L., *Ch. anthelminticum,* L. and
Ch. suffruticosum, Willd., yield anthelmintic volatile oils, whereas *Ch. spathulatum,* Sieb.
and *Ch. retusum,* Moq., are less important. — Van der Wielen[7]) stated that plants grown

        [1]) *Liebig's Annalen* 356 (1907), 212. — [2]) *Pharm. Weekblad* 58 (1921), 1080. As per a reprint kindly sent
us. — [3]) Cf. *Report* 1919, 113. — [4]) This is quite possible, as the distillation of American wormseed oil is
rather difficult and may lead to inferior products. Adulterations with ineffective substances are also frequent
and sometimes even absolutely valueless artificial mixtures are offered. Cf. *Berichte* 1921, 53, 1920, 63; *Report* 1919,
61, &c. — [5]) *Perfum. Record* 12 (1921), 39. — [6]) *Bull. des sciences pharmacologiques,* March 1921. — [7]) *Loc. cit.*

in India from seeds of the *Chenopodium ambrosioides* type yielded oils of varying efficacity. Whereas American oils are only lævorotatory ($a - 2°49'$ to $- 8°50'$, we have observed $- 4°$ to $- 8°50'$) the Indian oils had a rotatory power of from $- 2.34°$ to $+ 0.50°$[1]). 100 kilos of fresh herb, grown by the author in Amsterdam, yielded on distillation 5 grams of oil. After having been rectified *in vacuo* at 48° (55 mm.)? its index of rotation was $a + 0.74°$. By extraction with ether, van der Wielen obtained from Indian (Atjeh) chenopodium seeds an oil, the rotation of which was $a + 1.05°$. These experiments confirm Wirth's assertion that the rotation to the left increases if the oil is heated for some time[2]). Van der Wielen therefore thinks it probable that an oil of, *Chenopodium ambrosioides*, var. *suffruticosum*, Willd., obtained without heating to a higher temperature, would be dextrorotatory or inactive, but not lævogyrate[3]).

The author further calls attention to the fact that other physical properties of the oil likewise alter on heating. The specific gravity decreases, the index of refraction rises and the solubility in alcohol and acetic acid is lessened. The above-mentioned extracted oil of Atjeh seeds, for instance, had the following constants: d_{180} 1.008, n_{D180} 1.4735, soluble in 5.5 vols. of 60 per cent. acetic acid. As these constants resemble those of ascaridole rather much, and as *p*-cymene occurs in chenopodium oil, the author's opinion is that on heating the oil ascaridole is transformed into *p*-cymene, hydrogen being split off. The explosion-like decomposition of ascaridole when heated, noticed by Kremers, is supposed to support this theory.

Through experiments with animals, M. C. Hall and H. C. Hamilton[4]) have proved that the lower-boiling fractions of American wormseed oil have the same vermifugal efficacity as the higher-boiling constituents, without possessing the dangerous by-effects as cause inflammation and bleeding of the intestines. Tijssen[5]) was able to confirm these observations through clinical experiments. He prepared by distillation of an (Indian?) chenopodium oil (d 0.968) a fraction of the specific gravity of 0.951 and a residue of d 1.04. Both preparations were administered to patients suffering from hook-worm disease. In the first experiment the lower-boiling fraction resulted to be very efficacious, the higher-boiling one not. Later experiments had not quite the same result. Distillates free from ascaridole, administered three times in doses of 16 drops each, ejected 77 per cent. of the hook-worms, whereas the fractions containing ascaridole, given in the same quantities, destroyed 81 per cent. of the worms. The effect on ascaridæ was the same with either fraction.

According to van der Wielen the action of the different fractions on isolated intestinal worms ought to be determined, in order to refute the opinion now prevailing that oils of higher specific gravity are to be preferred to those of lesser density. Furthermore only the innocuous lower-boiling fractions of the oil ought to be used as remedies. The supposition would be very natural that the chief component of the lower boiling fractions, *p*-cymene, possessed the vermifugal properties[6]).

In the meantime another publication by Henry and H. Paget[7]) has appeared, in which they experimentally refute van der Wielen's above opinion. The authors examined Hall and Hamilton's assertion (see above) that not the ascaridole but the lower-boiling

¹) Cf. also the article of Henry and Paget, mentioned before, and *Bericht* 1921, 15. — ²) *Journ. Americ. Pharm. Assoc.* 9 (1920), 127; *Bericht* 1920, 61. We made the same observation many years ago. Cf. *Report* April 1908, 169. Cf. also Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. II, p. 360. — ³) This seems to be too hasty a conclusion. — ⁴) *Journ. of Pharm. and Exp. Therap.* 11 (1918), 231. — ⁵) *Gen. Tijdschr. voor Ned. Ind., Afl.* 1, *Deel* 61, 1921. — ⁶) Taking into consideration what other observers have stated, this judgment also seems a little hasty. — ⁷) *Pharmaceutical Journ.* 107 (1921), 349. As per *Pharm. Ztg.* 67 (1922), 126.

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fractions of the oil, the terpenes, are the efficacious constituents. They found that the vermifugal action was due exclusively to the ascaridole and not to the hydrocarbons. The products forming on decomposition of ascaridole in the heat were completely inefficacious.

E. K. Nelson[1]) publishes a method which makes it possible to determine quickly the ascaridole content of wormwood oil. It is based upon the solubility of ascaridole to the extent of 98 per cent. in a mixture of 60 parts of glacial acetic acid and 40 parts of water. The wormseed oil terpenes are insoluble in such a mixture. The test is carried out as follows: — 10 cc. of chenopodium oil are vigorously shaken in a cassia flask with 60 per cent. acetic acid. Then acetic acid of the same strength is added up to the mark, when the ascaridole content can be calculated from the quantity of undissolved oil. The author found like that in five samples from 48 to 73 per cent. of ascaridole.

Ch. Sparhawk[2]) gives an illustrated description of three varieties of American wormseed (*Chenopodium ambrosioides*, L., var. *anthelminticum*, Gray). The first, wild variety, a tangled mass of leaves, seeds, &c., does not produce much oil, although it feeds ravenously on the fertilizing material. A second, highly developed variety is distinguished by many seeds, with practically no leaves. This is the grade that produces the best oil, although the yield is not the largest. The third type, with stocky stem, plentiful leaves, and seeds on short stalks, gives the biggest returns, but the quality of the oil is not so good. Sparhawk adds that the seeds alone do not give any oil[3]) but that the percentage of seeds seems to indicate the quality.

The superiority of chenopodium oil over thymol in the treatment of hook-worm disease is described in a report of the Uncinariasis Commission to the Orient[4]). Whereas there was failure to cure the patient in 23.6 cases out of a hundred treated with thymol, there were only 7.6 failures with chenopodium. Apart from the many advantages, which we have pointed out before[5]) and the enumeration of which is therefore unnecessary, chenopodium oil has a disadvantage, according to the report in question, in that it often causes by-effects, such as dizziness, unsteadiness of gait, inability to rise, headache, &c. Certain purges intensified the toxic effects, thus giddiness and deafness were more marked among patients having castor oil than among those having magnesium sulphate.

W. Schüffner and H. Vervoort[6]) communicate that in British East India and the U.S.A. too large doses (3 cc.) of American wormseed oil were frequently given. Toxic effects (vomiting, dizziness, deafness, &c.) were often the result, so that the oil nearly lost its good reputation in these countries. In the same degree as the doses were gradually reduced (down to 1.2 grams), the bad by-effects ceased. According to the authors the age of the oil seems to have an influence on both efficacity and poisonous nature. Cajus and Mhaskar[7]) found that the ascaridole content went down from 70 to 56 per cent. in the course of one year. Wrench[8]) reports that a chenopodium oil which, after having been stored for one year still contained 66 per cent. of ascaridole, had lost its original noxiousness, but nothing of its efficacity. If Wrench's observations are correct,

¹) *Journ. Americ. Pharm. Assoc.* 10 (1921), 836. — ²) *Perfum. Record* 12 (1921), 388. — ³) Cf. Wirth's treatise (*Bericht* 1920, 60). Wirth proved that the oil is contained only in the hairs on the seeds and the leaves. — ⁴) *Perfum. Record* 12 (1921), 57. — ⁵) Cf. *Report* 1919, 113. — ⁶) *Mededeelingen van den burgerlijken geneeskundigen Dienst in Nederlandsch-Indië* 1921, 1, 29. — ⁷) *Indian Journ. of med. Research* 1920. — ⁸) *Ibid.* 1918.

oil that has been stored for some time would be preferable to the fresh product, as being less poisonous. — Schüffner and Vervoort recommend as a medium dosis three times 0.4 grams of chenopodium oil daily. Better results had been obtained with several small doses than by giving a larger quantity in one dosis. A laxative ought not to be given before, but after the cure. Anæmic persons should drink Karlsbad waters during the cure, which takes about five days. People suffering from kidney or liver complaints are very sensitive and should be treated with small doses only.

Chenopodium oil is said to have proved efficacious too as a remedy against tape-worms.

An article in the *Apothekerzeitung* also points out the danger of giving too large doses of American wormseed oil[1]. According to H. Brüning a dosis of 0.2 cc. per kilo of weight was deadly for dogs, smaller doses caused paralysis, for instance of the respiratory organs. The oil can be given pure or in emulsions and is said not to have the disagreeable by-effects produced by santonin. — Children ought to have as many drops as they are years old, but not more than ten, to be given after a little breakfast. Two hours later castor oil or another mild aperient should be given. The author proposes to include the remedy in the new edition of the German Pharmacopœia and to fix the maximum doses.

The following cases show that it is not superfluous to call attention to the noxiousness of chenopodium oil when given in large doses: —

A child of two years, who had taken 8 grams of wormseed oil, meant for an older brother or sister, died in spite of all medical assistance[2].

As per *The Perfumery and Essential Oil Record*[3] oil of chenopodium has been the cause of a fatality at the Hospital for Tropical Diseases, Endsleigh Gardens, London, N.W.

Regarding the production of chenopodium oil in Java see p. 80 of this *Report*.

Pharmacopœias.

Italian Pharmacopœia.

(*Farmacopea Ufficiale del Regno d'Italia, ed. IV.*)

The third edition of the Italian pharmacopœia, in use since 1910, has now been succeeded by a new one, the paragraphs of which concerning our articles we wish to deal with in the customary manner. Unfortunately, not much favourable can be said about them. Indeed, we could confine ourselves to a mere reference to our criticism of the former edition of the pharmacopœia (*Report* April 1910, 128) since the compilers deemed it unnecessary to do away with the numerous faults and mistakes of the third edition, and in the few cases where this was attempted it was performed rather unsatisfactorily. Here, the compiler of the paragraph ought to have realised that incorrect statements are of but little use in commercial intercourse, as they give rise to groundless objections and unnecessary correspondence. There was no difficulty in eliminating the existing errors, if one had taken pains to look out in the respective literature.

It may be taken for an effort to modernisation that with the essential oils notice has been taken of the direction of optical rotation, but since no limits have been

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[1] *Apoth. Ztg.* 36 (1921), 375. — [2] *Pharm. Ztg.* 66 (1921), 697. — [3] *Perfum. Record* 12 (1921), 185.

stipulated, this innovation is of hardly any use. In the subsequent discussion of the details, we have made up for this omission.

No new essential oil has been admitted; cajuput oil has been struck out.

In discussing the separate articles we follow the text of the pharmacopœia.

Anise Oil *(Essenza di anice).* — Colourless or yellowish; d_{200} 0.980 to 0.990; α_D to the left[1]); congeals on chilling to a crystalline mass which begins to melt at 15° and liquefies completely between 19 to 20°[2]); soluble in 2 to 3 vols. of 90 per cent. alcohol. Test for phenols with ferric chloride[3]).

[1]) The lævorotation amounts to − 2°.

[2]) Solidification must often be brought about by inoculating the chilled oil with some solid anise oil or anethole. Good quality oil begins to melt again above 17°. In case of careless storing, or after repeated melting the solidification point decreases constantly and the density increases. Comp. *Report* October 1904, 38.

[3]) This test is superfluous, since it traces a sophistication never observed with anise oil.

Cade Oil. — See Juniper Oil, empyreumatic.

Camphor *(Canfora).* — White, crystalline, translucent mass; d_{150} 0.993[1]); m.p.179°[2]); burns with a sooty flame; volatile already at ordinary temperature; hardly soluble in water (1 : 1200), readily in alcohol, ether, chloroform, acetic acid, fatty and essential oils. 0.1 g camphor must volatilise without leaving a residue; test for chlorine.

Natural camphor is optically active, synthetic inactive[3]).

[1]) This statement is quite useless, the more so as nothing is stated as to how this constant is determined. The value given is but only an approximate one.

[2]) In the 3rd edition the melting point was correctly given as 175°.

[3]) Under certain conditions, also the synthetic preparation is active; comp. *Report* October 1910, 197.

Cassia Oil. — See Cinnamon Oil.

Cedro Oil *(Essenza di cedro[1])).* — Greenish-yellow, the oil obtained by distillation being colourless[2]); d_{150} 0.857 to 0.861; α_D strongly to the right[3]); very sparingly soluble in water, soluble in about 5 parts of 90 per cent. alcohol[4]) and in every proportion in absolute alcohol.

[1]) Form the specific gravity required it follows that *lemon oil (essenza di limone)* is meant, since the various cedro oils (which are no articles of commerce) are partly heavier, partly lighter than stated above. Compare Gildemeister and Hoffmann, *The Volatile Oils*, 2nd edition, vol. III, p. 77.

[2]) Lemon oil is usually light yellow. Oils obtained by ordinary distillation are inferior and of no keeping quality.

[3]) The rotation amounts generally to +57 and +61°, oils occurring with higher or lower rotations. These data pertain to a temperature of 20°, this being important on account of the change of rotation with the temperature.

[4]) The solution, effected by 6 to 8 vols. of 90 per cent. alcohol, is often turbid due to the presence of mucous or vegetable wax-like substances.

Chamomile Oil *(Essenza di camomila comune).* — Blue, turning brown[1]) when exposed to the air, or when in contact with alcoholic soda solution. d_{150} 0.925 to 0.945; Roman chamomile Oil[2]) having d_{150} 0.905 to 0.915; soluble in 8 parts of 90 per cent. alcohol, opalescence occurring sometimes[3]); on chilling down to 0° it gets tough but does not solidify[4]).

[1]) Intermediately, the oil turns green.

[2]) It would have been better to quote this oil separately, as it behaves quite differently from ordinary chamomile oil. In discussing the other details of this paragraph, we take only the latter oil into consideration.

[3]) In consequence of its high content of paraffins, the oil gives but turbid mixtures with 90 per cent. alcohol.

[4]) This statement is incorrect, chamomile oil being, at 9°, a comparatively solid mass.

Cinnamon Oil (Cassia and Ceylon Cinnamon Oils) *(Essenza della cannella).* — Colourless or light yellow, turning gradually into yellow or brown[1]); soluble in 3 parts of 70 per cent. alcohol[2]); d_{150} with Ceylon oil 1.024 to 1.040; α_D to the left[3]); d_{150} with

Cassia oil 1.055 to 1.065[4]). Reactions with nitric acid and with ferric chloride; percentage of cinnamic aldehyde not below 70[5]).

[1]) Cassia oil is from the beginning dark yellow to brown; neither of the two ·cinnamon oils are colourless.

[2]) With cassia oil, the solution is in most cases not quite clear.

[3]) Up to —1°, rarely higher. With cassia oil, the rotation amounts up to —1° and +6°.

[4]) The upper limit is given too low, it must read 1.070.

[5]) This does not apply to either of the oils. With Ceylon cinnamon oil, the aldehyde content amounts to 65 to 76 per cent.; with cassia oil, the lowest value is at least 75 per cent.

Clove Oil *(Essenza di garofani)*. — Yellowish, turning gradually brown when exposed to the air; $d_{15°}$ 1.045 to 1.070; soluble in 2 parts of 70 per cent. alcohol; eugenol percentage at least 85 when tested with 5 per cent. caustic potash solution[1]); identity reaction and test for absence of phenol[2]).

[1]) The amount of caustic solution required by the pharmacopœia is insufficient. This fact has equally been pointed out by V. Massera *(Riv. Ital. delle essenze e profumi* 3, Jan. 12, 1921; acc. to *Chem. Zentralbl.* 1922, II. 171) who suggests to shake, in a cassia flask, 10 cc. oil with 100 cc. 3 per cent. caustic soda solution.

[2]) Adulterations of clove oil with phenol have never been observed hitherto. A note on the rotation might have been useful, clove oil rotating to the left, up to —1° 35′.

Eucalyptole *(Eucaliptolo)*. — Colourless; $d_{15°}$ 0.930[1]); b.p. 176 to 177°; solidifies, in a freezing mixture, to a crystalline mass which remelts at —1°[2]); identity reaction with bromine; when mixed with the same volume of carbon disulphide eucalyptole must yield a clear mixture (test for water); test for phenols with ferric chloride[3]).

[1]) The specific gravity ranges between 0.928 and 0.930.

[2]) Eucalyptole melts at about +1°. If necessary, congealing must be started by rubbing the glass walls with a glass rod.

[3]) This test is unnecessary, on the other hand, it might have been pointed out that eucalyptole must be inactive.

Eucalyptus Oil *(Essenza di eucalipto)*. — Light yellow[1]), on exposure to the air it turns brown and resinifies; $d_{15°}$ 0.910 to 0.930; α_D faintly to the right[2]); soluble in 3 vols. of 70 per cent. alcohol; percentage of eucalyptole not below 70, tested by the resorcinol method[3]).

[1]) Eucalyptus oil is colourless, pale yellow, or pale greenish.

[2]) The rotation amounts up to +15°.

[3]) The pharmacopœia prescribes our *original* test of shaking 10 cc. oil with 90 cc. of a 50 per cent. resorcinol solution. Since sometimes too high figures are obtained hereby, we later on modified the method. Compare *Reports* April 1908, 50 and October 1915, 20.

Juniper berry Oil *(Essenza di ginepro)*. — Colourless or faintly greenish yellow, thickening on exposure to the air and light and turning then more yellow; $d_{15°}$ 0.865 to 0.885[1]); soluble in 9 parts of 90 per cent. alcohol[2]) and in 1 part of carbon disulphide[3]).

[1]) The lower limit is given too high, it must read 0.860.

[2]) Only freshly-distilled oils answer this requirement; the solubility decreases rapidly.

[3]) A possible turbidity is caused by a slight content of water due to the preparation of the oil. Here, too, a reference might have been made to the optical rotation, the latter being to the left and amounting usually up to —13°, rarely higher.

Juniper Oil, empyreumatic (Cade Oil) *(Olio cadino)*. — Dark brown; $d_{15°}$ 0.99 to 1.05; sparingly soluble in water to which it imparts an acid reaction; soluble in ether, chloroform, and absolute alcohol; miscible with carbon disulphide and benzine only with turbidity; about 65 per cent. of the oil must distil between 150 and 300°; identity reactions.

Lavender Oil *(Essenza di lavanda)*. — Colourless[1]), faintly yellow or green; $d_{15°}$ 0.882 to 0.895; α_D to the left; soluble in 3 parts of 70 per cent. alcohol; percentage of linalyl acetate, at least 35; test for absence of citric ester[2]).

[1]) Only the rectified oils are colourless, these, however, being of inferior quality. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 434, footnote 2.

[2]) The rotation ranges between — 3 and — 9°.

[3]) This test should have been extended to other esters which may likewise be present besides ethyl citrate. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 441 and *Bericht* (German) 1920, 39.

Menthol *(Mentolo)*.—Colourless prisms; m. p. 44°[1]); b. p. 212°[2]); nearly insoluble in water, most readily soluble in alcohol, ether, chloroform, and carbon disulphide, soluble in fats and paraffin oil; 0.1 g. menthol must not leave behind a weighable residue when evaporated on a water bath; test for absence of thymol[3]).

[1]) A certain allowance must be granted, *i. e.*, 42 to 44°.

[2]) Menthol boils under 753 mm. at 215°, the mercury thread being wholly surrounded by the vapours.

[3]) Since mixtures of menthol and thymol are liquid this adulteration is highly improbable.

Methyl Salicylate *(Salicilate de metile)*.—Colourless; soluble in alcohol, ether, paraffin oil, fatty and essential oils; scarcely soluble in water: d_{150} 1.182 to 1.187[1]); b. p. 218 to 221°. On shaking with water the volume of the ester must not decrease to a noticeable extent (test for absence of methyl or ethyl alcohol); identity reaction with ferric chlorides.

[1]) The limits are incorrect, the specific gravity ranging between 1.185 and 1.190 (15°).

Mustard Oil, natural and artificial *(Essenza di senape)*.—Colourless, afterwards yellowish with a tinge of red; b. p. 148°[1]); d_{150} with the artificial oil 1.020, with the natural oil 1.018 to 1.025[2]); $\alpha_D \pm 0°$; readily soluble in alcohol, ether, and carbon disulphide, sparingly soluble in water (1:1000); identity reactions; percentage of *iso*-thiocyanallyl, 94 to 99.

[1]) This requirement must read correctly, mustard oil boils *for the greater part* between 147 and 153°.

[2]) This statement is likewise incorrect; the specific gravity of the artificial oil is between 1.020 and 1.025, that of the natural oil between 1.014 and 1.025 (15°).

Orange Blossom Oil *(Essenza di fiori d'arancio amaro)*.—Yellow, turning reddish under the influence of air and light; blue fluorescence; d_{150} 0.870 to 0.880; α_D to the right[1]); soluble 1 to 2 parts of 90 per cent. alcohol; on adding more opalescence ensues[2]).

[1]) French neroli oil, the chief commercial product, rotates between +1°30' and +9°8', Spanish oil between +9°30' and +29°, Italian oil between +2°54' and +56°30'; the two last-named oils are, however, in all probability no pure distillates from the flowers of the bitter orange.

[2]) This statement applies for 80 per cent. alcohol; in 90 per cent. alcohol, orange flower oil is clearly soluble in every proportion. After some time, however, slight opalescence sets in owing to a separation of paraffin.

Peppermint Oil *(Essenca di menta)*.—Colourless, straw-yellow, or greenish, on exposure to the air turning gradually yellow and viscous; d_{150} 0.890 to 0.920; d_{150} of the Italian oil 0.908 to 0.925; α_D strongly to the left[1]); English oil dissolves in 3 to 5 volumes of 70 per cent. alcohol, Italian oil gives with about 2 volumes sometimes a slightly opalescent solution which does not become clear on further dilution[2]); solidifying at — 8 to — 20° with separation of menthol, Italian oil does not solidify even at —17°; colour reaction with glacial acetic and nitric acids[3]); test with iodine for absence of turpentine oil[4]).

[1]) The rotation ranges between — 20 and — 34°, with Italian oils between — 2°30' and — 26°51'.

[2]) American oils which, to judge from the specific gravity, are equally official, give generally a faint opalescence of the solution; with English oils this is sometimes likewise the case.

[3]) We consider it decidedly a failure to comprise such a reaction (to which even otherwise normal English oils do not always answer) amongst the requirements of a pharmacopoeia. The quality of an oil musts never be judged by this reaction. It would have been far more correct to require a definite minimum content of menthol which with good commercial oils is not below 50 per cent.

[4]) This test is entirely superfluous, quite obsolete, and absolutely useless, and ought to have been abandoned in the prior editions.

Rosemary Oil *(Essenza di rosmarino).* — Colourless or yellowish-green; d_{150} 0.90 to 0.92; soluble in 10 parts of 90 per cent. alcohol[1]).

[1]) Rosemary oil dissolves already in one-half volume of 90 per cent. alcohol.

Sandalwood Oil *(Essenza di sandalo).* — More or less yellow; d_{150} 0.975 to 0.985[1]); a_D to the left[2]); soluble in 5 parts of 70 per cent. alcohol; santalol ($C_{15}H_{24}O$) content not below 90 per cent.[3]).

[1]) The lower limit should be 0.973.

[2]) The angle of rotation lies between — 16 and — 20°.

[3]) This minimum content does not agree with the statements given in the pharmacopœia as to the estimation of santalol which correspond to a content of 87.26 per cent.

Terpine Hydrate *(Terpina idrata).* — Lustrous, colourless and odourless prisms; on drying in a vacuum or above sulphuric acid it loses about 9.5 per cent. water; soluble in about 250 parts of cold, in 32 parts of boiling water, or in 10 parts alcohol, insoluble in light petroleum; the aqueous solution must show neutral reaction; terpine hydrate melts at 116°, terpine at 102°[1]); on boiling the aqueous solution acidified with sulphuric acid a smell of hyacinths[2]) is produced; 0.1 g. terpine hydrate must burn without leaving a residue.

[1]) Terpine melts at 104 to 105°.

[2]) In this reaction, terpineol is formed which, however, smells of lilac and not of hyacinth.

Thymol *(Timolo).* — Colourless, translucent crystals; m. p. 49 to 50°[1]); b. p. 228 to 230°[2]); sparingly soluble in water (about 1:1200), the aqueous solution must show neutral reaction; soluble in less than 1 part of alcohol, ether, acetic acid, chloroform, and fatty oils; soluble in 2 parts of 10 per cent. caustic soda solution; melted thymol floats on water, solid thymol drops down; 0.05 g. thymol, when heated on the water-bath, must volatilize completely; identity tests and test for absence of phenol.

[1]) The m. p. lies between 50.5 and 51.5°.

[2]) Thymol boils, under 753 mm. pressure, at 232°, the mercury thread being fully surrounded by the vapours.

Turpentine Oil *(Essenza di trementina).* — Colourless; boiling range, 155 to 162°; d_{150} 0.860 to 0.877; a_D to the right or the left according to the origin of the oil[1]); perfectly volatile; hardly soluble in water, soluble in 12 parts 90 per cent. alcohol, 7 vols. 94 to 96 per cent. alcohol, in every proportion of absolute alcohol, ether, chloroform, carbon disulphide, fatty and essential oils[2]); resinifies when exposed to the air; neutral reaction; when kept in a bottle but partly filled the oil turns yellow and shows acid reaction.

For certain purposes, the crude oil is admitted, which is colourless or faintly yellow and leaves on evaporation a residue of 2 per cent.[3]).

In addition, old, so-called ozonised oil must be kept for use, which colours blue a paste of starch and potassium iodide.

[1]) The rotation ranges between + 41° and — 35°.

[2]) Possible turbidity is caused by a small amount of water in the oil owing to the distillation process. On addition of a desiccating substance, *e. g.*, sodium sulphate, such turbidities disappear instantaneously.

[3]) This evaporation must be performed with special precautions, as otherwise too high values may result. Compare Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 20.

Chemical Preparations and Drugs.

Benzaldehyde. — In our last *Bericht*[1]) we accurately described our method of quantitative determination of chlorine in benzaldehyde. The apparatus then shown in the picture, and supplied by the Leipzig firm of F. Hugershoff, has meanwhile been slightly modified.

Both the U-tubes serving as absorbing vessels have been provided with a short pipe each which can be closed by means of a piece of rubber tubing and a pinch-cock, so that the absorbing liquid can now be more easily removed. Furthermore, the glass tube connection the two U-tubes has been provided with a small bulb, as sometimes the liquid of the first U-tube passed over into the second.

In addition we would mention the fact that the air in the laboratories is liable to contain hydrochloric acid gas and that then even passing it through dilute silver nitrate solution may not free it entirely from chlorine. We therefore connect the apparatus with the fresh air outside by means of a glass tube passed through a small opening in a window.

As previously mentioned[1]) we consider the indication of "benzaldehyde, technically tree from chlorine" as a nuisance, liable to cause confusion to the detriment of the honest dealer. Our opinion has since been confirmed, for its is almost incredible what stuff is frequently offered under above designation. There are products of all shades, from a slight to the most pronounced chlorine reaction, and it is only a matter of how elastic the conscience of the supplier may be for terming the product "technically" or, as it is now called, "commercially free from chlorine".

Out of the many samples which have been examined in our analytical laboratories we would only mention one, just to show what amount of cheek some suppliers have. The constants were as follows: $d_{15°}$ 1.0633, $\alpha_D + 0° 6'$, $n_{D20°}$ 1.54054, completely insoluble even in 10 volumes of 50 per cent. alcohol, acid v. 12.5 = 2.7 per cent. benzoic acid, chlorine reaction: extraordinarily strong. This shows that the article was absolutely unsatisfactory, not a single one of the constants coming up to the requirements for benzaldehyde. It is even too bad for a crude product, as results from the defective solubility and the excessive specific gravity, which latter cannot be explained by an excess of benzoic acid, into which benzaldehyde may be converted by oxidation. These two properties referred to induced us to examine the sample a little more closely, as far as the small quantity permitted. It resulted that the product contained only 68 per cent. of benzaldehyde. The quantity at our disposal was not large enough for further investigation regarding the admixtures, &c.

W. von Rechenberg[2]) prefers Beilstein's copper oxide test for chlorine in benzaldehyde to the well-known combustion method. After comparative tests, he ascribes more exact results to the former.

We have stated on previous occasions[3]) that, in our opinion, the combustion method is decidedly more accurate and reliable than the copper oxide test, and we

[1]) *Bericht* (German) 1921, 56. — [2]) *Chem.-Ztg.* 45 (1921), 627. — [3]) *Report* April 1912, 151.

still adhere to this standpoint. We consider Beilsteins's test as useful only for general guidance, and it seems risky to us to deduce binding conclusions from it in all the cases, as owing to the perceptible volatility of the copper benzoate the flame may be coloured green by the benzoic acid, which would lead to erroneous conclusions[1]). We would therefore recommend caution when judging benzaldehyde by the result of the copper oxide test.

As to catalytic reduction of benzaldehyde with copper, and the pyrogenous decomposition of benzaldehyde, see pages 131 and 146 of this *Report*.

Benzylalcohol. — According to D. J. Macht and A. T. Shohl[2]) solutions of benzylalcohol keep their anæsthetic qualities unchanged when kept in ampoules of unattackable glass, and their hydrogen ion concentration varies but very showly. On the other hand, in glass which gives off alkali the solutions loss their anæsthetic power quickly and show alkaline reaction in the course of several months.

J. Messner[3]) gives the following explanation for the decomposition of benzylalcohol which is said to pass off also in neutral or feebly acid (acetic or hydrochloric acid) solution: — Apparently, reduction as well as oxidation takes place simultaneously, one molecule of the alcohol losing oxygen with formation of toluene, a second molecule absorbing the oxygen liberated with formation of benzaldehyde and water: $-2C_6H_5CH_2CH = C_6H_5CH_3 + C_6H_5CHO + H_2O$. This reaction may be accelerated by action of light, or owing to the presence of organic or inorganic impurities in the water or the benzylalcohol. The latter can even be its own catalyst, as has been proved by Jacobson. Messner strongly disapproves that aqueous solutions of benzalcohol, which decompose easily, be traded in ampoule fillings.

By heating benzylalcohol, in xylene solution, with barium sulphate + palladium K. W. Rosenmund and F. Heise[4]) obtained 5 per cent. benzaldehyde, 12 per cent. benzyl ether, 50 per cent. benzylalcohol, and 20 per cent. undistillable residue. Pure barium sulphate was of no influence on the alcohol.

The action of the benzyl esters on the human or the animal organism may be attributed either to the unchanged benzyl ester molecule or to the benzylalcohol formed in the body by hydrolysis of the ester. The fact that benzyl acetate and benzoate are excreted as hippuric acid and that benzylalcohol has a relaxing effect on the unstriped muscle seems to indicate that the effect is due to the hydrolysis of the esters[5]). Hence, it would be rather probable that the therapeutic effects would be proportional to the rates of hydrolysis of the esters. This possibility induced E. H. Volwiler and E. B. Vliet[6]) to investigate the chemical part of the problem and to compare the rates of hydrolysis of a number of benzyl ethers. Their experiments, which were conducted according to the directions of Bischoff and Hedenström[7]), proved that the rates of hydrolysis of the esters, under identical conditions, increase in the following order: — salicylate, benzoate, stearate, cinnamate, acetate, succinate, and fumarate. In benzyl acetylsalicylate, the rate of hydrolysis is of the same order as in benzyl salicylate.

The authors give a description of the methods employed for the preparation of some of the esters. The preparations had the following constants: — fumarate, m. p. 58.5

[1]) Cf. Kunz-Krause, *Apotheker-Ztg.* **30** (1915), 141. *Report* October 1915, 56. — [2]) *Journ. of Pharm. and exper. Therap.* **16** (1920), 61. As per *Therap. Halbmonatsh.* **35** (1921), 216. — [3]) *Pharm. Zentralh.* **63** (1922), 1. — [4]) *Berl. Berichte* **54** (1921), 2042. — [5]) Macht, *Journ. Pharmacol.* **11** (1918), 263. — [6]) *Journ. Amer. chem. Soc.* **43** (1921), 1672. — [7]) *Berl. Ber.* **35** (1902), 3433.

·to 59,5°, b. p. 210 to 211° (5 mm.); salicylate, b. p. 170 to 175° (7 mm.); cinnamate, m. p. 33 to 34°, b. p. 228 to 230° (22 mm.); acetylsalicylate, m. p. 25.5 to 26.0°, b. p. 197 to 200° (7 mm.).

Benzyl Benzoate. — E. C. Mason and E. C. Pieck[1]) did not notice any change worth mentioning in the respiration of dogs after an intravenous injection of 2 cc. of 10 per cent. benzyl benzoate solution; breathing became flatter after an injection of 4 cc., the blood pressure decreased and the contractions of the pylorus became feebler. The latter ceased altogether after an injection of 6 cc. (the breathing stopped at the same time, causing death). The solution had only a slight effect on the tension of the small intestine; lage doses may cause hearth failure. The action on the uterus was very feeble, the increase of the pressure in the artery of the lungs inconsiderable, whereas no extension of the bronchioles could be proved.

According to E. A. Heller and E. Steinfield[2]) daily injections, repeated for four days, of 1 cc. each and one injection of 1.5, 2 and 2.5 cc., respectively, of benzyl benzoate per kilo of weight had no effect on the number of white corpuscles in rabbits. After larger doses the animals became sleepy and faint, one of them died.

Bromostyrene. — Theoretically, three monobromostyrenes substituted in the side-chain are possible, *i. e.*, the two stereoisomerides with the formula Ph·CH : CHBr and the body Ph·CBr : CH₂. Two isomerides are hitherto known, namely one ω-bromostyrene Ph·CH : CHBr (A) and the α-bromostyrene Ph·CBr : CH₂ (B). Ch. Dufraisse[3]) succeeded in obtaining the third isomeride, the other ω-bromostyrene (C), from bromobenzalacetophenone and powdered caustic soda: m. p. — 8 to — 7°; b. p. 71° (6 to 7 mm.); d₂₀₀ 1.426; n$_{D22.50}$ 1.5990. Phenylacetylene resulted as by-product. Furthermore, the author obtained, by heating sodium dibromohydrocinnamate with sodium carbonate, according to Nef[4]), the well-known ω-bromostyrene (m. p. + 6 to 7°[5]); b. p. 107° (22 to 23 mm.); d₂₀₀ 1.422; n$_{D20.50}$ 1.6094), and from phenylacetylene and hydrogen bromide, α-bromostyrene, m. p. — 43°; b. p. 71° (7 to 8 mm.); d₂₀₀ 1.406; n$_{D19.50}$ 1.5881.

With alcoholic potash solution the three bromostyrenes yield phenylacetylene. The bodies A and C, on treatment with bromine, gave rise to identical tribromostyrenes Ph·CHBr·CHBr₂, m. p. 37 to 38°; thus the constitution of the three bromostyrenes as given above is proved to be correct.

The two geometrical isomerides of the m. p. + 6 to 7° and — 8 to — 7°, according to observations by the same author[6]), undergo most readily a mutual but partial rearrangement under the influence of sun-light. Strangely, the stable form (m. p. + 7°) obtains equilibrium sooner than the other modification. The mixture of the isomerides, when equilibrium is reached, melts at + 2° and shows the same odour as the stable form.

On exposure to the air, α-bromostyrene is readily oxidised to bromoacetophenone. Since freshly-distilled α-bromostyrene shows no irritating action on the mucous membranes, Dufraisse[7]) is of opinion that the irritation caused by older preparations must be ascribed to the presence of bromoacetophenone.

¹) *Journ. of Laborat. and Clin. Med.* 6 (1920), 62. As per *Chem. Zentralbl.* 1921, III. 495. — ²) *New York med. Journ.* 112 (1920), 160. As per *Chem. Zentralbl.* 1921, I. 507. — ³) *Compt. rend.* 171 (1920), 960. — ⁴) *Liebig's Annalen* 308 (1899), 267. — ⁵) With our own preparations we observed: — sol. p. ± 0 to 2.5°; the m. p. stated above must therefore be regarded with some suspicion. — ⁶) *Compt. rend.* 172 (1920), 67. — ⁷) *Ibidem* 172 (1921), 162.

Camphor. — D. A. Wallace and S. B. Plumer[1]) determined the amount of camphor in camphorated oils by heating the solution in cotton-seed oil for three hours, that in pea-nut or olive oils for four hours and that in sesame oil for five hours up to 120° and calculated the camphor content from the loss in weight. Camphorated oils are oxidized on heating and increase in weight. This increase in weight, which has been determined by the authors in certain cases, has to be taken into account when calculating the camphor content.

The authors further recommend the already known method[2]) of determining the the camphor content in camphorated oils by means of the optical rotation.

Castoreum. — At the annual auction in London, the Hudson Bay Company offered in December 1921 2649 lbs. of Canadian castoreum, of which 575 lbs. were sold. Of the Oregon quality 2932 lbs. were available, of which 1170 lbs. were disposed of[3]).

Coumarin. — According to a process invented by W. Ponndorf[4]) coumarins are obtained by condensing phenols or phenol ethers with fumaric or maleic acids under the influence of condensing agents such as zinc chloride, or aqueous or alcoholic 73 per cent. sulphuric acid, at a temperature not below 120°. The condensation of fumaric acid with phenols passes off by union of a hydrogen atom in *ortho* position of the phenol with one of the two COOH-groups of the acid, with formation of formic acid, and by ring-formation of coumarin from the resulting coumaric acid.

T. Yanagisawa and H. Kondo[5]), in preparing coumarin, make use of iodine as catalyst, and obtained, when boiling salicylic aldehyde, acetic anhydride, and sodium acetate for four hours in an oil both, a yield of 70 per cent. crude coumarin.

G. C. Bailey and F. Boettner[6]), when endeavouring to prepare methylcoumarin from malic acid and *m*-cresol, found the method devised by Fries and Klostermann[7]) to be the most successful one. They obtained the highest yield (54 per cent.) of methylcumarin when malic acid was added slowly to a the mixture of *m*-cresol and sulphuric acid heated to 135°, the reaction product then poured on ice, and the precipitate formed taken up in 50 per cent. alcohol and crystallised from this solvent. A *m*-cresol of 84 per cent. yielded about 40 per cent. of methylcoumarin.

Toxicity tests carried out with mice proved methylcoumarin to be not more than one-tenth as toxic as coumarin. As to the perfume value, dilute solutions of methylcoumarin were said to be of almost the same odour as those of natural coumarin. The odour of the dry crystals, however, was considerably less intense than with natural or synthetic coumarin.

Eucalyptole. — The cresineol method for the determination of cineole devised by T. Tusting Cocking[8]) gives, according to recent statements[9]) of the author, satisfactory results if the amount of cineole present in the sample reaches 45 per cent. and upwards. When the amount of cineole present falls below 45 per cent. the method must be modified insofar that a certain amount of pure cineole, or an equivalent amount of

[1]) *Americ. Pharm. Journ.* 98 (1921), 600. — [2]) Cf. *Reports* April 1915, 73; 1918, 92. Some angles of rotation are given for the oils mentioned, with and without camphor. — [3]) *Oil, Paint and Drug Reporter* 101 (1922), No. 1, p. 32. — [4]) Germ. Pat. 338737, published July 4, 1921; *Chem. Zentralbl.* 1921, IV. 1224. — [5]) *Journ. pharm. Soc. Japan* 1921, no. 472; *Chem. Zentralbl.* 1921, III. 958. — [6]) *Journ. ind. eng. Chem.* 13 (1921), 905. — [7]) Cf. *Report* October 1906, 96. — [8]) Comp. *Bericht* (German) 1921, 65. — [9]) *Perfum. Record* 12 (1921, 339.

pure cresineol is added to the oil before carrying out the determination. The result is calculated by means of a table, with due regard to the cineole or cresineol added.

According to this modified method the author tested a series of oils with low cineole content, with the following results: —

	Percentage esters	Percentage cineole
Lavender oils, French . . .	29 to 52.7	18.0 to 22.6
„　　　„　English . . .	6.2 „ 10.7	23.6 „ 27.4
Spike oils	2.3 „ 3.9	33.2 „ 39.0
Rosemary oils, French . . .	3.1 and 4.1	23.2 and 25.4
„　　oil, Spanish . . .	2.5	19.4

We abstain from discussing the correctness of these figures, yet we find the quantity of cineole found by Cocking in the French lavender oils remarkably high. According to our own observations[1]), French lavender oils contain only very small amounts of cineole, and we come to the conclusion that Cocking must have dealt with adulterated, or highly impure oils. Should this not be the case, the results would certainly not speak in favour of the cresineol method, which, too, was originally devised for different purposes. In such a case, the statements concerning the cineole content of the other oils would have to be regarded with some doubts.

Gum Benjamin. — A. Mayrhofer[2]) examined a gum benjamin offered by a Vienna firm as Palembang benzoin and sent in tins of 15 kilos. The drug which ought to alter quickly its appearance when the pieces are broken and left in contact with the air, consisted of reddish-gray to gray-brown pieces which easily crumbled and showed on some larger surfaces the impression of white pieces of tissue. The neighbouring pieces of gum were gray or blackish. The main part of the substance was composed of pieces of wood, held together by a whitish or brownish-red, glossy mass. After exhaustive extraction with alcohol there was a residue of 52 to 68 per cent. No cinnamic acid was present (test with potassium permanganate). As to benzoic acid, 3.1 per cent. = 9 per cent. of the part soluble in alcohol, were obtained. The alcoholic extract had the following constants: acid v. 99.9 (determined indirectly), saponification v. 198.1 (determined in the cold). The microscopic examination of the pieces of bark showed that they originated from a Styracea.

The available data were therefore not sufficient to characterize the drug as Palembang benzoin, especially because the mother plant and origin of this commodity are not known well enough so far[3]). Nevertheless the article is said to have a certain value, as it may be useful, for instance, for preparing benzoin tincture.

Heliotropin. — The oxidation of *iso*safrole to heliotropin is considerably favoured by the addition of amino-carboxylic acids. On the strength of this fact C. Sievers and L. Givaudan & Co.[4]) publish a process, consisting in that 120 parts of *iso*safrole are oxidized at a medium temperature with a solution of either sodium bichromate

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[1]) Comp. *Report* October 1898, 27. For safety's sake, we endeavoured to prove or determine, with four lavender oils of warranted purity, the cineole present and arrived at the result, in accord with our former experiences, that lavender oil contains but so little cineole, that the proof of its presence causes some difficulty. There is absolutely no possibility that pure lavender oils contain such an amount of cineole as stated by Cocking. — [2]) *Apotheker Ztg.* 86 (1921), 821. — [3]) According to Lüdy and Tschirch Palembang benzoin is exported from Palembang in Sumatra; Dieterich mentions as mother-plant a *Styracea* of Further India, about which nothing definite is known. — [4]) Swiss Pat. 91087, Oct. 17, 1921. Addn. to 89053. Cf. p. 99 of this *Report*.

(240 : 1000) or chromic acid, in the presence of 10 parts of p-amino-benzoic acid, dissolved in 480 parts of 50 per cent. sulphuric acid. By way of the bisulphite compound one obtains 15 parts of unaltered *iso*safrole and 90 parts of heliotropin.

Menthol. — The list of articles which the Board of Trade considered dutiable under the Safeguarding of Industries Act includes menthol. We do not know what prompted the competent authorities to take this remarkable step, as an article is concerned which cannot possibly be made in England. Anyway this proceeding has roused a storm of criticism in the affected quarters in England[1]), so that the Board of Trade tried to get out of all difficulties by adding the letter "R" to menthol, which signifies that the chemical indicated is included only when it is "pure", "puriss.", "extra pure", "B. P.", &c. In criticizing this measure the *Chemist and Druggist* gives vent to the following opinion: "There is no specially purified menthol obtainable in commerce, except as a laboratory curiosity, and then it has no superiority over ordinary menthol." If the author knew that purified, *i. e.* recrystallized menthol is sold in ton lots on the continent and that, contrary to what may be the case in England, Germany and a good many other European countries use nò other menthol at all for pharmaceutical purposes, he would surely have given a different verdict.

Further communications on menthol are to be found under the heading of Japanese Peppermint Oil, page 58 of this *Report*.

Musk. — Chungking is the chief port of original export for musk, which is brought into Szechwan from Tibet, says Consul P. R. Josselyn, Chungking[2]). During the ten years from 1893 to 1902 the average yearly export through the Maritime Customs at Chungking was 3971 pounds, while during 1918 the amount exported was only 948 pounds. This decline was partly due to the war; but for the last 15 years there has been a steady decline, which would indicate that the musk deer is no longer as plentiful or as easily caught as formerly[3]). Probably considerably less than one-half of the musk that comes into China from Tibet is exported abroad. The remainder is used locally by the Chinese medicine shops and as a perfume.

Before the war France took approximately 50 per cent. of the export, the United States being second, taking about 20 per cent. During the five years from 1910 to 1914 the average yearly export to the United States from all China was 406 pounds, valued at 120284 Haikwan taels[4]). During the three years 1915 to 1917, inclusive, it increased to 613 pounds, valued at 195087 Haikwan taels.

Musk, artificial. — According to A. Reclaire[5]) a "new brand of musk", received from France, contained no less than 82 per cent. acetanilide. For the quantitative determination of this well-known adulterant of artificial musk the author proceeded as follows, basing his method on the prescriptions given by A. Seidel[6]) and J. C. Tonus[7]): —

The acetanilide is decomposed by boiling it with 20 per cent. hydrochloric acid. The aniline formed is converted into tribromo-aniline by means of an excess of potassium bromide-bromate solution of known strength. After having added some potassium iodide solution, the excess of bromine is titrated back with sodium thiosulphate solution, when the content of aniline (acetanilide) can be calculated from

[1]) *Chemist and Druggist* 95 (1921), 875. — [2]) *Americ. Perfumer* 16 (1921), 106. — [3]) Cf. *Bericht* (German) 1920, 72. — [4]) As to the altered value of the Haikwan tael see *Bericht* (German) 1920, 73. — [5]) *Perfum. Record* 12 (1921), 280. — [6]) *Journ. Americ. chem. Soc.* 29 (1907), 1091. — [7]) *Physisch-chemisch onderzoek van verbindingen, gevormd uit een amine en een organisch zuur* (Leiden 1918).

the difference. This method is said to be sufficiently accurate for technical purposes (difference 0.4 to 0.6 per cent.).

O. Wichmann[1]) examined trinitroisobutyltoluene and trinitrobutylxylene as to their pharmacodynamic action. In the human or animal organism, by oxidation of the CH_3 group, the trinitrobutyltoluene splits off water which joins the butyl group. In this way tertiary butyl alcohol is formed in addition to m-trinitrobenzoic acid. The latter combines with glycocol, thus forming m-trinitrohippuric acid which is secreted with the urine. The tertiary butyl alcohol has the capacity of combining in the animal organism with glycuronic acid which also leaves the body with the urine. The human organism secretes the tertiary butyl alcohol through the respiration process.

In a closed room, insects (gnats and flies) were killed by the effect of artificial musk.

A subcutaneous injection of 0.05 to 0.1 gram of trinitrobutyltoluene dissolved in oil caused the death of cold-blooded animals (frogs) after four hours.

Warm-blooded animals were not affected by up to 1 gram taken internally. After a subcutaneous injection of 0.2 gram dissolved in oil an increase of the reflex movements was noticed in guinea-pigs; 0.4 gram caused death within 12 hours after previous signs of paralysis.

Doses up to 1 gram, internally, had no effect on human beings; but it is to be supposed that larger quantities injected subcutaneously must act as poison on the human organism.

A therapeutical use of trinitrobutyltoluene and trinitrobutylxylene is not very likely to come into consideration.

Myrtole. — The myrtle oil fraction boiling between 160 and 180° is used for inhaling under the name of myrtole. One of its essential components, which causes perhaps its praised antizymotic and desodorizing effect, is eucalyptole. This consideration apparently induced the supplier of a so-called myrtole, submitted to us for inspection, to give eucalyptole instead, a proceeding requiring a rather elastic conscience.

The sample behaved as follows: — $d_{15°}$ 0.9294, $\alpha_D \pm 0°$, $n_{D20°}$ 1.45802, solidification point $+0.2°$, soluble in 4 volumes and more of 60 per cent. alcohol. These constants tally completely with those of eucalyptole ($d_{15°}$ 0.928 to 0.950, $\alpha_D \pm 0°$, $n_{D20°}$ 1.454 to 1.459, solidification point between 0 and $+1°$, soluble in 4 volumes and more of 60 per cent. alcohol, whereas those of myrtole are entirely different, as is shown by the following figures established for myrtole of our own distillation: — $d_{15°}$ 0.884 to 0.904, $\alpha_D +15$ to $+24°$, $n_{D20°}$ 1.462 to 1.463, soluble in 0.5 volume and more of 90 per cent. alcohol, sometimes already in 80 per cent. alcohol (1 to 2 volumes).

The difference in price between myrtole and eucalyptole is so considerable, that above supplier's tactics paid well, even if he sold his "myrtole" very cheap.

Nitrobenzene. — We mentioned in our last *Bericht*[2]) that freshly marked linen caused symptoms of poisoning in babies. We are now told[3]) that they were not due to nitrobenzene, but to aniline.

In two cases of acute poisoning with nitrobenzene, due to "Jamaica gingers" containing this body, R. F. Loeb, A. V. Bock and R. Fitz[4]) examined the blood. Methæmoglobin was not present; the oxyhæmoglobin in the arterial blood was reduced to 6.2

[1]) *Dissertation*, Bonn 1921. As per *Apotheker-Ztg.* 36 (1921), 510. — [2]) *Bericht* (German) 1921, 67. — [3]) *Deutsche med. Wochenschr.* 47 (1921), 1526. As per *Chem. Zentralbl.* 1922, I, 480. — [4]) *Americ. Journ. of the Med. Sciences* 161 (1921), 539. As per *Chem. Zentralbl.* 1921, III, 968.

(240:1000) or 8 per cent., the capacity of binding oxygen to 8.9 and 6.2 per cent., respectively. dissolved in $\frac{4}{6}$e was moderate leucocytose and, for six hours, anuria. In the urine p-amino-one obtainsnol was present.

A further case of poisoning mentioned was brought about by resorption through Menie skin (the garments had been soiled with oil containing nitrobenzene).

As to the detection of nitrobenzene in bitter almond oil, see page 6 of this *Report*.

Peru Balsam. — A balsam of Peru, sent us for examination, was greatly adulterated or rather resulted to be a composition, but was termed genuine by the supplier, who refused to take it back, in spite of the repeated reclamations of the buyer. As the supplier was a large concern and in a position, no doubt, to have the article properly examined, this case is a perfect riddle for us. If one had taken the trouble to look into the matter, the determination of the specific gravity would have revealed already that there was something the matter.

Said balsam behaved as follows: — d_{150} 1.1387, cinnamein content 63.6 per cent., ester v. of the cinnamein 225.4, nitric acid test = bluish green colouring. There could not be any question of a pure, genuine balsam. Its specific gravity and the ester v. of the cinnamein were too low; besides, the cinnamein differed from the normal product in that it was not liquid at room-temperature, but semi-solid. The nitric acid test, leading to a golden yellow colouring in the case of genuine balsam of Peru, also indicated adulteration.

For any expert the stuff would have been suspicious on account of its odour and abnormally light colour. It is therefore remarkable, that the supplying concern in question did not notice anything. Needless to say that such a concoction does not answer the requirements of the pharmacopœia.

Peru Balsam, artificial. — We have taken up the manufacture and are pleased to state that our product meets with increasing popularity.

Bark of Rhamnus Frangula. — Through steam distillation of the bark of *Rhamnus Frangula,* O. A. Oesterle[1] obtained 0.05 to 0.1 per cent. of a crystalline substance of strongly fusty smell, which had probably formed only during the distillation. The product contained, apart from dark coloured impurities, small quantities of a white crystalline body, insoluble in soda solution; a compound precipitated in the form of a jelly from hot soda solution; a body soluble in soda lye, crystallizing from water in radiate form, and a compound insoluble in soda lye, crystallizing from alcohol in the shape of brownish yellow scales. This inodorous and tasteless substance had the empiric formula $C_{15}H_{12}O_4$, m. p. between 100 and 101°.

Resin of a Peruvian Styracea. — E. Maldonado[1] examined a resinous substance, known in the Province of Cuzco (Peru) by the name of *incienso macho* and frequently used for incense, perfumery and medical purposes. The drug comes probably from a variety of *Styrax* (*Styrax ovatum,* A. DC., occurs in the valleys of Cuzco, Umbara Valley) and forms irregular, hard, reddish-black or black masses. They are covered with a greenish dust and taste aromatic at first, then sharp. The fractured surface exhibits a brilliant, vitreous, yellow colour. The odours recalls that of vanilla. The

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[1] *Bol. Farm. de Lima* of June 30th, 1920. As per *Chemist and Druggist* 95 (1921), 207.

author prepared from the drug a gum, an oxydase, vanillin, a small quantity of aromatic esters, and 5 per cent. of benzoic acid.

Thymol. — The Badische Anilin- und Sodafabrik in Ludwigshafen publish a method of preparing thymol from *m*-cresol[1]). The *m*-cresol is sulphonated, and the resulting *m*-cresol-sulphonic acid treated with *iso*propyl alcohol and sulphuric acid (preferably concentrated) in the warmth. The sulpho-group is split off the mass at a temperature of from 120 to 125°, the thymol being distilled off simultaneously. The oil thus obtained, which is almost completely soluble in dilute soda lye, is treated in the usual way and subjected to fractionated distillation. The first runnings contain the unaltered cresol, then the thymol passes over, whereas the last fraction contains probably an isomeride of thymol, crystallizing from benzene in large crystals (m. p. 114 to 115°).

The preparation of thymol from cymene has repeatedly been patented already[2]). R. M. Cole[3]) suggests as a further improvement the electrolytic reduction of nitro-cymene and the subsequent diazotisation and reduction of the 1-methyl-2-amino-4-*iso*-propyl-5-hydroxybenzene. The diazo-group is then replaced with hydrogen in the usual way.

Nothing is mentioned in the discussions as to the yield.

By condensation of one molecule of salicylaldehyde and two molecules of thymol in the presence of some dilute sulphuric acid, F. Lavilla Llorens[4]) obtained hydroxy-phenyldithymylmethane $OH \cdot C_6H_4 \cdot CH : (C_6H_2 \cdot CH_3 \cdot OH \cdot C_3H_7)_2$, m. p. 185°; methylether, m. p. 137 to 138°; ethylether, m. p. 77 to 78°. In these compounds all the three hydroxyl-groups reacted. Tribromo derivative, m. p. 170°; iodine derivative, m. p. 111°. By double interaction of the alkali derivatives with metal salts the lead, copper and iron compounds were obtained.

According to R. Maire[5]) the following three species of *Ptychotis* occur in North Africa: — 1. *Ptychotis Ammi,* L. = *Sison Ammi,* L. = *Seseli ammoïdes,* L. = *Ptychotis ammoïdes,* Koch, a small annual plant occurring so abundantly in fallow ground that one might think it was cultivated. This umbelliferous plant, found in all southern Europe, is easily recognized by its smooth, naked stems and leaves, its petiolate pinnules and its white inflorescences provided with dimorphous bracts but without any involucre. 2. *Ptychotis trachysperma,* Boiss. = *P. aspera,* Pomel., is distinguished from the former by its wrinkled fruits and its spatulate bracts. It occurs in western North Africa and in Spain. 3. *Ptychotis atlantica,* Coss., a perennial flowering late and occurring frequently in the higher mountains (Tell Mountains in the departments of Algiers and Constantine; Aurès Mountains). All the parts of these plants smell strongly of thymol, especially the fruits, and might perhaps be used for the manu-facture of this phenol.

Brocq-Rousseu[6]) mentions that horses can stand internal doses of 0.22 to 0.25 gram of thymol per kilo. From 0.20 gram upwards symptoms of paralysis occur. The symptoms of poisoning are faintness, ataxy, fall of temperature and often paralysis of

[1]) *D.R.P.* 350809 of July 4th, 1920. — [2]) Cf. *Berichte* (German) 1920, 77; 1921, 74. — [3]) *Perfum. Record* 12 (1921), 281. *Chem. Zentralbl.* 1921, IV. 513. — [4]) *Ann. Soc. Espanola Fis. Quim.* [2] 18 (1920), 139. As per *Chem. Zentralbl.* 1921, III. 785. — [5]) *Parfum. moderne* 14 (1921), 79. — [6]) *Compt. rend. soc. de biologie* 84 (1921), 257. As per *Chem. Zentralbl.* 1921, III. 125.

the hind-legs. If the thymol stays for any length of time in the stomach or in the intestins, it irritates the mucous membranes. Aristol (dithymoldiiodide) is soluble in water and in the gastric juice.

Vanillin. H. C. Sievers and L. Givaudan & Co.[1]) publish a method of preparing vanillin from acetylisoeugenol by oxidation with sodium bichromate or chromic acid, in the presence of amino-carboxylic acids. The addition of 1.5 to 2 per cent. of such a amino-carboxylic acids as catalyst, for instance p-amino-benzoic acid, has a favourable influence on the oxidation and on the yield of vanillin. One proceeds as follows: 120 parts of isoeugenol are distributed in 1240 parts of a sodium bichromate solution (250 parts in 1000 parts of water); under continuous stirring at a temperature of 80°, a solution of 1.5 to 2 parts of p-aminobenzoic acid in 500 parts of 50 per cent. sulphuric acid is allowed to flow in. As soon as the oxidation is completed the acetylvanillin formed is extracted with a solvent and the vanillin obtained by way of the bisulphite compound. One obtains 12 parts of unaltered acetisoeugenol and 68 parts of vanillin.

The yield is the same if the amino-carboxylic acids are replaced by aromatic amino-aldehydes, such as p-amino-benzaldehyde[2]).

As to the manufacture of vanillin from guayacol and formaldehyde, see page 143 of this *Report*.

Two samples of vanillin tested in our laboratories were grossly adulterated; one containing about 55 per cent. of antifebrin, the other 75 per cent. of benzoic acid. The adulterants influenced the melting point considerably, of course, for the preparation containing antifebrin melted already between 64 and 68° (instead of at 82°), whereas the other began to sinter at 68° and was completely melted only at 110°.

The antifebrin was separated off by shaking the product, dissolved in ether, with soda lye, when only the vanillin is taken up by the soda lye. The antifebrin remained in the ether and was obtained by evaporating the solvent, it was recognized by its melting point (113 to 114°) and by its isonitril reaction.

The benzoic acid was separated in a similar way, only that in this case the vanillin was removed from the ethereal by shaking it with bisulphite lye. The residue obtained on evaporation of the ether melted at 121° and could be identified as benzoic acid also by its other properties.

Taking into consideration the difference of price between vanillin and these two adulterants, one easily understands that the buyers of the article will have paid far too much for it in spite of the apparently low price.

The methods of vanillin determination in vanilla extracts[3]), according to which lead acetate is added to the dealcoholized extract and the aldehyde is the determined by weight, often lead to inexact results. Either the vanillin obtained is not quite pure and the figures are too high, or the purification causes losses. The method indicated by Hiltner[4]), who purifies the vanillin in the end through sublimation at 105°, is not perfect either, as according to H. J. Wichmann[5]) the aldehyde forms non-volatile decomposition products, when heated for some length of time to the above temperature. Wichmann heated pure vanillin for 3 to 6 hours at 105 to 108°, and obtained 4 to 5.6 per cent. of non-volatile, yellowish-brown residues, most likely oxidation and decomposition pro-

[1]) *Swiss Patent* 89053 of April 16th, 1921. — [2]) *Swiss Patent* 91088 of October 17th, 1921. Supplement to 89053. — [3]) The alcoholic extract of vanilla is meant. — [4]) *U. S. Bur. Chem. Bull.* 152 (1912), 135; 162 (1913), 83. — [5]) *Journ. Ass. Offic. Agric. Chem.* 4 (1921), 479.

ducts of a complex nature. This indicates that the errors caused by the sublimation of the vanillin according to Hiltner's method, are considerable in the case of vanilla extracts containing more than 0.2 per cent. of vanillin.

Winton and his co-workers devised a lead number, now the official A. O. A. C. method, for analyzing vanilla extracts. In Wichmann's[1] opinion it is not free from objection and he therefore publishes a new method of determining the lead number, supposed to simpler and more reliable.

To 175 cc. of boiled water in a liter flask Wichmann adds 25 cc. of 8 per cent. lead acetate solution and 50 cc. of vanilla extract, removes the alcohol by distillation, adds dilute sulphuric acid to the diluted and filtered residue and calculates the number of grams of metallic lead in the lead sulphate precipitated. This figure doubled is the required lead number.

Doherty[2] says that the gravimetric determination of vanillin in vanilla essences can be avoided by a method based upon the reaction of the aldehyde with sodium bisulphite and the colour reaction with bromine water and ferrous sulphate. The author states that it is reliable and easily carried ont with the aid of Duboscq's colorimeter. A detailed description is given in the *Chemiker-Zeitung* 45 (1921), 687.

Thiercelin and Violet[3] give the following information regarding the solubility of vanillin: Vaselin dissolves 11, glycerin 7 and oil 11 per cent. of vanillin at the ordinary temperature.

Solubility of Vanillin per litre.

Temperature	Water	Alcohol			
		15 per cent.	30 per cent.	60 per cent.	90 per cent.
10°	5,2 grams	50 grams	80 grams	755 grams	1100 grams
20°	15,5 „	66,6 „	180 „	1500 „	1750 „
50°	44,4 „	166,6 „	750 „	3000 „	5000 „
78°	66,6 „	400 „	950 „	4000 „	10000 „

We found the following proportions[4]: —

Solubility of Vanillin in 100 parts by weight of the solvent at 10°.

Alcohol 96 per cent.	Alcohol 70 per cent.	Glycerin	Olive Oil	Liquid Paraffin
38 grams	30 grams	1 gram	0.9 gram	less than 0.1 gram

The vanilla crop in Madagascar, Comores and Réunion, amounting to 500 tons on an average, is estimated at only 350 tons for 1921. It is supposed that the United States consume 35, France 25, England 10, Switzerland 8, Scandinavia 8 and Germany, Holland and Spain together 14 per cent. of the crop[5].

The following data are taken from an article on vanilla production in Mexico by Ch. H. Cunningham[6]: — At present Mexico employs over 50000 people in the cultivation and extraction of vanilla. Vanilla (*Vanilla planifolia*, Andr.) is indigenous to the soil of Mexico[7]. It is principally cultivated in the districts of Papantla and Misantla in the State of Vera Cruz, the most productive region lying south-east of Tuxpan, between

[1] *Americ. Perfumer* 16 (1921), 301. — [2] *Journ. and Proceed. Royal Soc. of New South Wales* 57, p. 157. — [3] *Parfum. moderne* 14 (1921), 153. — [4] *Report* April 1909, 144. — [5] *Drug and Chemical Markets* 9 (1921), 405. — [6] *Commerce Reports,* of November 20th, 1920. As per *Americ. Journ. Pharm.* 93 (1921), 272. — [7] Preuss considers the wild Mexican vanilla to differ from *Vanilla planifolia. Berichte d. Pharm. Ges.* 11 (1901), 24.

the rivers Nantla and Tuxpan. French colonists who settled on the banks of the Nantla river in the 19th century learnt the cultivation of vanilla from the natives and were soon successful. (According to Preuss[6]) the plantations were in a bad state in 1900 but have been enlarged continuously since.) The vanilla grows best in rich, sand soil, not drained too thoroughly, at an altitude of 1000 feet above sea-level. It is sheltered by the trees of the forest or by trees planted for that purpose.

There are different varieties of vanilla in the vicinity of Misantla. They are not so plentiful nor are they considered so good as the Papantla beans. These indigenous varieties are the *cimarror*, the *mestiza* and the *mansa*. When they are cured, only an expert can distinguish between the various classes. There is also a wild bean known as vanilla *platano*, which the Indians eat. This differs from the ordinary vanilla in that the plant is much smaller but has larger leaves.

In order to avoid plundering of their crops, the planters cut the vanilla early, sometimes in October and November instead of in January and February. As a result the beans weigh a pound less per thousand than they would normally.

For commercial purposes vanilla is divided into four classes: *grande fina* (20 cm.), *chica fina* (10 to 15 cm.), *zacata* and *basura*. The former two differ only in length, whereas their weight is almost the same. The *zacata*, which is a larger bean than the former two, grows more abundantly along the roadsides in the warm and hot regions of Mexico, where formerly it was considered to be without commercial value.

The exports from Mexico were as follows: in 1912/13 = 288766 kilos to the value of 3315471 Pesos; 1918 = 45066 kilos to the value of 505020 Pesos; 1919 = 197403 kilos to the value of 2333264 Pesos.

According to W. M. Doherty[1]) Mexican vanilla beans average 2 per cent., Java and Bourbon beans about 2.75 to 2.9 per cent. of vanillin. Tahiti vanilla is but of little value in comparison, as it contains only 0.6 to 0.7 per cent. of vanillin.

Guadeloupe vanilla is generally classed among the inferior kinds[2]) although it may come very near the Mexican product if properly treated. As Ch. A. Smeltzer[3]) states the Guadeloupe planters have generally not cured the beans carefully enough nor in the proper way, so that their commercial value suffered. The Guadeloupe vanilla begins flowering in March, at which time the flowers are fecundated by the natives, who use a small wooden instrument (similar to a tooth-pick). Quite often the natives fecundate too many flowers on the same raceme with the result that the beans are apt to be thin and short. Another disadvantage is that the native planters gather the beans often immature (it takes about nine months for the vanilla to ripen). When thoroughly cured, this immature vanilla will result in a dry, ordinary quality bean; but the average curer, who is curing for weight and not for quality, permits the moisture to remain in the bean, with the result that his product reaches the market in apparently good condition, but soon gets mouldy. On the other hand, the fully-matured bean will never lose its good quality.

Frequently the beans are cured in Guadeloupe by the hot water method, which involves the smallest loss in weight. However, only the Mexican or sweating method, introduced in the island already 30 years ago by M. Fox, leads to a first class vanilla. Smeltzer has the beans assorted first and then "needled". This is done by making four scratches on the outer surface of the bean from end to end, deep enough to break through the skin, in order to permit the moisture to escape. This enables the bean to

[1]) *Journ. and Proceed. Royal Soc. of New South Wales* 57, p. 157. As per *Chem. Ztg.* 45 (1921), 696. — [2]) Cf. *Reports* April 1902, 100; October 1909, 142. — [3]) *Americ. Perfumer* 15 (1921), 197.

cure uniformly within as well as without. About 10 o'clock in the morning woolen blankets are spread on cement terraces, which by this time have become hot from the sunshine, each blanket being capable of holding about 25 kilos of green beans. Weather permitting, the various sized green beans are spread on the blankets and allowed to remain until 2 p. m. Then they are wrapped up in the blankets, folded tightly and turned upside down. After an hour's heating in this manner, the bundles are deposited in "sweating boxes" specially made to hold 500 kilos and not to permit any of the heat to escape. After 48 hours the boxes are opened and the vanilla is carefully gone over for mouldy beans. The others are again taken to the terraces, placed on other dry blankets and again given the sun. This heating and sweating process is repeated from eight to ten times, until the beans give off no more moisture and are sufficiently cured. The finished beans are dried on wire trays for two weeks, then assorted and packed into tins lined with wax paper.

Notes on Scientific Research in the Domain of the Terpenes and Essential oils.

General.

In a paper on the Oils, Fats and Waxes in Latin America, O. Wilson[1]) gives a description of the principal essential oils manufactured in these countries. For the most part thuy are the products of the tropical regions of northern South America, Mexico, Central America, and the West Indies, the value of which products is but small compared with the resources. In Mexico, linaloe oil is distilled from the wood and also the seeds of various species of *Bursera*, in French Guiana the Cayenne linaloe oil from "bois de rose femelle", a strong-smelling wood said to derive from *Ocotea caudata*, Mez., a lauracea, and likewise the so-called Guiana sandalwood oil from wood originating apparently also from different lauraceæ[2]). A similar oil, the so-called West Indian sandalwood oil, derived from the rutacea *Amyris balsamifera*, L.[3]), has been shipped to Europe for over a century. It has been used as adulterant of, and substitute for, genuine sandalwood oil. The West Indies furnish furthermore orange oil (Jamaica), pressed and distilled oil of limes (Montserrat, Jamaica, Dominica), bay oil (Jamaica, St. Thomas, Guadeloupe, Antigua, Barbados, and Dominica), and pimento oil (Cuba, Haiti, Trinidad, San Domingo, Antigua, Leeward and Windward Islands, and Jamaica). The evergreen pimento tree, *Pimenta officinalis*, Lindl., also occurs in Mexico, Costa Rica, and Venezuela. Other possibilities of Jamaica, not yet developed, include vetiver and camphor. In Paraguay, the great number of bitter orange trees are made use of for the preparation of bitter orange oil and, to a limited extent, also of neroli oil. Another tree, the zygophyllacea *Bulnesia Sarmienti*, Lor., growing in Paraguay and Argentina, yields the important guniac wood oil, called erroneously also "champaca" oil[4]).

Other essential oils and materials from which they can be distilled cover a wide range throughout the tropical forests of the Amazon and Orinoco Valleys and French Guiana. In Brazil, the leaves of a plant called "false jaborandi", *Arthante geniculata*, Miq. *(Piperaceœ)*, yield a light-greenish oil of spicy mint-like odour and pungent burning taste; the leaves of *Citrosma oligandra*, Jul. *(Monimiaceœ)*, called in Brazil *"catingueira"*, furnish an oil with a greenish fluorescence and an odour resembling bergamot. The leaves of the wild lemon, *Citrosma cujabana*, Mart. *(Monimiaceœ)*, contain an oil with an odour of bergamot and lemon, and those of the wild coffee tree, *Citrosma Apiosyce*, Mart., an oil with a lemon-like odour. From the bark of *Dicypellium caryophyllatum*, Nees, *"Cassia caryophyllata"*, an oil is obtained containing eugenol and having a clove-like odour. In Bolivia, a grass grows abundantly which is closely related to lemon-

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[1]) *Chem. and met. Eng.* 24 (1921), 1101. — *Bull. of the Pan-Amer. Union*, October 1921, 334, where the same article is published with two additional illustrations (evidently drawings) of the Paraguay petitgrain oil industry which are omitted in the *Chem. & met. Eng.* — [2]) Cf. *Report* October 1911, 80. — [3]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. III, p. 114. — [4]) Genuine champaca oil has entirely different qualities and originates from *Michelia Champaca*, L.

grass and citronella grass and yields an oil similar to that of vetiver. In British Guiana and Brazil, the branches of the *priprioca* tree *(Ocotea preciosa,* Nees, *Lauraceæ —* female *priprioca*[1])) contain an oil somewhat resembling linaloe oil. From Brazil, Venezuela and Colombia, copaiba balsam, from Salvador largely balsam of Peru, and from Colombia principally balsam of Tolu are exported. Mexico and Central America yield oil of turpentine. Finally, we mention vanilla and tonka beans which are grown in Mexico and the West Indies, and in Venezuela, Trinidad, Tobago, the Guianas, and Brazil respectively.

The National Committee on medicinal plants and plants yielding essential oil and extracts growing in Italy and the Italian colonies published a report[2]) on its activities in 1915 to 1919. The Committee was formed at the beginning of the war in order to propagate the cultivation and utilization of medicinal plants in Italy. The report enumerates the following plants, the cultivation of which come under consideration:— Peppermint, calamus, common and Roman chamomile, cherry laurel, lavender, balm (melissa), rosemary, thyme, valerian, anise, cumin, eucalyptus, fennel, rose, sage, and violets.— In the surroundings of Naples, and in general on the south coast, *inter alia,* various rose varieties such as *Rosa Hayi, R. Brünner, R. damascena, R. centifolia, R. Drusky* were cultivated. Since the cultivation would appear to pay — the oils extracted with ether were very fragrant —, it is intended to be continued. From fennel seed, melissa and laurel leaves, the blossoms of *Origanum vulgare,* L. and the leaves of *Lippia citriodora,* H. B. et K., the Institute of pharmaceutical Chemistry at the Naples University obtained, by distillation, a good yield of the essential oils.

A publication by W. W. Stockberger[3]) deals with the cultivation of drug plants in the United States. In numerous places in the Central and Eastern States the following drug plants have been found to thrive well:— anise, belladonna, caraway, chamomile, conium, coriander, digitalis, dill, elecampane, fennel, henbane, horehound, sage, stram-onium, tansy, and thyme. — Aconite, arnica, lovage, poppy, senega, valerian, and worm-wood seem to thrive best in the northern part of the U. S. where the rainfall is well distributed. On the other hand, cannabis, licorice, and wormseed are better suited to the warmer climate of the South. — Alethris, althaea, angelica, calamus, orris, pinkroot *(Spigelia marilandica,* L.), peppermint, serpentaria, and spearmint are adapted generally for situations where the soil is rich and moist, but lavender and larkspur prefer well-drained sandy soil. Ginseng and goldenseal *(Hydrastis canadensis,* L.) occur naturally on rich soil in the partial shade of forest trees. In addition to the plants mentioned, the following have further been cultivated:— cascara sagrada, castor-oil plant, *Pyrethrum cinerariaefolium,* Trev., *Lobelia inflata,* L., parsley, pokeweed, safflower, saffron, vetiver, wintergreen, and wormseed.

In a paper entitled, "Michigan, an important source of raw vegetable products", H. Kraemer[4]) reports on cultivation experiments started with about 50 drug plants in the botanical garden of the university of Michigan. As the experiments turned ont satisfactorily, Kraemer advocates a more extensive cultivation of the plants in Michigan. Of aromatic plants, spearmint and, above all, peppermint have been cultivated in that State. The peppermint oil industry, the development and history of which the author relates in full, started originally in Wayne County, New York, and was introduced into Michigan, Indiana, Ohio, and other states later. The climate and soil of Michigan

[1]) Cf. *Report* April 1911, 87. — [2]) *Federazione pro Montibus, Pubblicazione* N° 94, Rome, 1921. — [3]) *U. S. Dep. Agr., Farmer's Bull.* 663, August 1920. — [4]) *Mich. Acad. Sci. Report* No. 21, 1919. As per a reprint kindly forwarded to us.

proved to be particularly favourable for the growing of peppermint, and the oil industry, therefore, developed here preferably well. The world's annual production of peppermint and spearmint oil amounts to about 600,000 lbs. Of this quantity, America — and principally Michigan — produces nearly one-half. Each acre yields about 30,000 lbs. of the green herb, which when distilled furnish to the utmost 100 lbs. of oil.

As to the origin of the peppermint industry, Kraemer's narrative runs as follows:— About 75 years ago there was a Yankee pedlar named Burnett who went through the country districts of Connecticut, Massachusetts, Vermont, and New York peddling tin-pans, rugs, chromos and other articles coveted by the farmer's families. The women had not a great deal of money, so Burnett hit upon a scheme of exchanging herbs in lieu of money for his merchandise. In the course of his travels he secured such quantities of peppermint so as to distil the oil by constructing numerous stills, especially in Wayne County, New York; he then gave up his peddling business and devoted himself to collecting and distilling the mint. Seeing the success of Burnett, a dealer H. G. Hotchkiss[1]) became interested in the peppermint oil industry, sold the oil (not touched by American drug dealers) to Hamburg realising thereby a good profit, and soon started to work on an extensive scale. The farmers of Wayne County followed his example, and in a short time the industry spread throughout the county.

A preliminary statement of the general results of the 1919 census of manufactures, for the essential oil industry of the United States, has been issued by the Bureau of the Census, U. S. Department of Commerce[2]). In 1919, 77 establishments (1914 : 103) produced essential oils (not included are synthetic and artificial oils) valuing $ 4411775 ($ 1289361). In Michigan, 29 establishments were located in Michigan, 22 in Indiana, 9 in Connecticut, 5 in New York, 4 in New Jersey, 3 in Pensylvania, 2 in Virginia, and 1 each in California, Kentucky, Ohio, and Tennessee.

According to the Census for 1920[3]), the total quantity of flavours produced in 1920 in the U. S. showed a reduction by 73 per cent. compared with the production in 1919, due principally to a greatly diminished output of saccharin and coumarin. New flavours reported in 1920 were benzyl acetate, benzyl cinnamate, cinnamyl pro-pionate, ethyl cinnamate, methyl phthalate, and "vanilidine".

The production of perfume materials was 99470 lbs., valued at $ 332008 (138 per cent. gain compared with the value in 1919). The number of preparations increased from 24 to 41. The following were reported for the first time in 1920: — acetophenone, anisic aldehyde, cinnamic aldehyde, diphenylmethane, ethyl benzoate, ethyl phthalate, isobutylphenyl acetate, methyl benzoate, methylethyl acetate, methyl cinnamate, methyl-indole, phenylpropyl acetate, styrene, isobutyl salicylate, methyl guaiacol, benzylidene acetone, and p-cresol methyl ether.

We cull the following statements from a report[4]) of the Experimental Station for aromatic plants in Madagascar, located in Iroloina, near Tamatave, near the eastern coast of the island.

The cultivations in Nossi-Bé of the ylang-ylang tree started some years ago[5]) but given up later on have been started afresh in the last years although the blossoms are considered to be inferior to the Manila blossoms. Quite recently, the geranium, *Pelargonium roseum,* Willd. has been cultivated in Madagascar, hithertho with good

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[1]) H. G. H. is to-day one of the oldest American trade marks, but it comprises only crude oil. — [2]) *Drug and chem. Markets* 8 (1921), 1055. — [3]) *Census of dyes and coal-tar chemicals* 1920, 49. — [4]) As per *Heil- und Gewürzpflanzen* 4 (1921), 126. — [5]) Cf. *Report* October 1909, 124.

success. From the Moramanga and Fianarantson districts, large quantities of geranium leaves are exported. In the island of Mayotte belonging to the Comoro Islands, in the north-west of Madagascar, the cultivation of mint, sage, verbena[1]), and especially patchouli has been started.

The clove tree, *Caryophyllus aromaticus*, L., is very common in Madagascar, particularly in the rainy district of Ste.-Marie, Movrantsatra, and Tamatave. In 1918, 200 tons of cloves were exported from Ste.-Marie.

The principal export commodity of Madagascar is the vanilla bean, which is cultivated in the north-western coast and the volcanic districts of the island, in Nossi-Bé, and the Comoro Islands. In Antalaka, on the northern coast of Madagascar, the annual turnover of vanilla amounts to 100 tons. In order to drain the fever districts and to protect other cultivations, the eucalyptus tree, *E. Globulus*, Lab. has been successfully grown in many parts of Madagascar. Likewise, nutmeg trees (*Myristica fragrans*, Houtt.) are cultivated in several places of that island.

Of wild-growing aromatic plants of Madagascar, the following may be mentioned: — the hazamalanga tree, the fruit of which is said to contain an oil with a strong aromatic oil[2]); *Ravensara aromatica*, Gærtn., a lauracea with aromatic leaves and bark; *Angræcum fragrans*, Thou., an orchidea, the leaves of which, smelling of coumarin, are used for scenting tea; finally, a *Canarium* species with a fragrant resin.

According to an article in *The Chemist and Druggist of Australasia*[3]), the large plant installed by G. J. Adcock in New South Wales for the preparation of the essential oils of orange, lemon, lavender, geranium, and peppermint appears to meed with good success. Wages in Australia are low compared with those in other countries, and a further advantage is the encouragement given by the Excise regulations which permit the use of duty-free Australian spirit provided it is converted into the primary perfume by adding other Australian products so as to effectively denaturise the spirit.

Some thirty-five years ago the Victorian Government established a "perfume farm" which was at first remarkably successful, but owing to lack of interest on behalf of the new Goverment, turned out a failure after some time. A sad mistake, too, was that the French methods for obtaining oils had been copied, *e. g.* the "enfleurage à froid" process, withouth due regard to their suitability for Australian products, and even without exact knowledge how these processes were to be carried out properly.

According to a note in the *Chemiker-Zeitung*[4]), the Spanish distillers of essential oils refrain from distilling large quantities of oils, more especially of thyme oil, owing to their unfavourable financial situation, and the slow demand of Spanish oils ruling since October 1920. The principal buyers of thyme oil are the Americans who prefer the oil of *Tomillo carasqueno*, a *Corydothymus* species growing in Southern Spain and rich in carvacrol, while the French patronise the oil from *Tomillo rojo* (*Thymus vulgaris*, L.) with but 20 to 47 per cent. of phenols, of which 30 to 35 per cent. thymol.

A question in this respect was kindly answered by Mr. Felix Gutkind[5]), Malaga, as follows: — The statements in the *Chemiker-Zeitung* are perfectly correct. Only very little rosemary oil has been distilled; but this oil can be distilled at any time of the year, except in the months with excessive rainfall, so that the stocks, when scarce,

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[1]) From the abstract available it is not clear whether it is the case of the true verbena, *Lippia citriodora*, H. B. *et* K., or of the so-called Spanish verbena, *Thymus hyemalis*, Lange. — [2]) From hazamalanga wood, Bois de Cass, originating from *Hernandia peltata*, Meissn. of Madagascar we obtained years ago 1.03 to 2.06 per cent. oil with an odour of perilla aldehyde. The oil obtained from the *fruits* (0.5 per cent.) did not show this odour. — [3]) *Chemist and Druggist* 95 (1921), 48. — [4]) *Chem.-Ztg.* 45 (1921), 776. — [5]) Letter of Aug. 31, 1921.

can be renewed within a short time. The only question is whether the cutters are willing to suffer a reduction of their wages as long as the victuals remain so dear in Spain. In many cases, rosemary oil has been sold to foreign countries with loss or at least without profit merely with the object to secure means for distilling thyme oil, the yield of which was likewise very low as compared with former years.

France and equally England, it is true, have purchased a good quantity of oil rich in thymol, since both countries make use of thymene (? a mistake in lieu of thymol). The U. S. are and were buyers of *Corydothymus* oil sampled to you recently. Much of this oil is also shipped to Grasse. In the preceding years, the bulk of the oil from *Thymus vulgaris* in Spain has been worked up for thymol production.

As to the result of the yield of spike oil, nothing definite can be said as yet. High-priced stocks from 1920 still exist. The 1921 crop will most certainly be but one-fourth of the 1920 one, and the 1921 production is most probably to be limited by the owners of old stocks with the view to justify the high price of the old crop as soon as a lively demand appears.

As per a report of the Administration of Mysore[1]) for the year ending June 30, 1920, a number of satisfactory essential oils are distilled there. Important results were obtained in the distillation of cardamoms. Nearly two tons of patchouli leaves were distilled, and the oil was used for perfumery purposes. Qualitative experiments were done in the distillation of rosha grass, vetiver, lemongrass, citronella grass, *Kasturi arsina*[2]), and ajowan seeds.

J. A. Hugues[3]) gives a description of an apparatus serving for *extracting the odorous principle* with volatile solvents from plants, roots, leaves, flowers, even from gums (!) and resins. Two endless movable chains circulate within the extraction pan and carry a series of boxes which travel continuously from top to bottom and *vice versa*, as in a dredging machine. The extractor contains a sufficient quantity of liquid, such as light petroleum, carbon disulphide, or ethyl chloride, so that the lowest box at a time is completely submersed in the solvent. The bottom, lid, and the side walls of each box are perforated. The boxes are then filled with the drugs for extraction and worked continually through the solvent until the latter is saturated with the perfume. The major part of the solvent is then drawn off by means of a pipe at the bottom of the still, and by distillation the liquid is separated into solvent and odorous residue. The solvent retained by the drug may recovered by steam-distillation of the boxes. Owing to the low loss of solvent this process seems to be preferred to other methods[4]).

A. Koehler[5]) has constructed a contrivance for abstracting automatically the odorous principle from flowers. The flowers are fed from a hopper on a circulating greased belt running over two cylinders. After a certain time the flowers are stripped off from the belt.

The recovery of essential oils from the distillation waters by cohobation is stated, in a communication by J. de Lorgues[6]), to have been introduced in Southern France about ten years ago by Charabot and Laloue. We beg to point out that in the Barrême factory, erected by Schimmel & Co. in 1905, this well-known process has been made us of in the distillation of lavender oil.

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[1]) *Americ. Perfum.* 16 (1921), 107. — [2]) We were hitherto unable to ascertain what is meant by *Kasturi arsina*. Probably, it is the case of *Kasturi arishina = Curcuma aromatica*, Salisb., or *Kasturi bhendi = Hibiscus Abelmoschus*, L. (Cf. Dymock, Warden, and Hooper, *Pharmacographia Indica*, 1890.) — [3]) French Pat. 505085, Oct. 1, 1920. — [4]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 247. — [5]) French Pat. 518713, May 30, 1921. As per *Chem. Zentralbl.* 1921, IV. 596. — [6]) *Perfum. Record* 12 (1921), 143; *Chemist and Druggist* 94 (1921), 855.

In the same article, a second process, devised by Gattefossé, is described for recovering essential oils from the distillation waters. The aqueous distillate passes in a very fine spray a layer of rectified petroleum in a closed vessel about one-third full. The water is fed from above, gives off its oil content to the hydrocarbon, separates at the bottom of the vessel and is siphoned off. This washing process is repeated several times. The oil obtained after evaporating the solvent is not nearly of the same quality as the oil resulting from direct distillation.

Another process for recovering the essential oils suspected in the distillation waters has been patented by J. Amic, L. Roure, J. Roure, and P. Magiapan [1]). The water being separated from the oil in a receiver is conducted to the upper part of a distillation-column filled with coke pieces where it meets the vapours ascending from the still. The condensed liquid is siphoned off, while the vapours leaving the column are cooled in a condenser and then conducted to the receiver for separation.

As to the "water oils" of various plants, we refer to pp. 48, 50, 58 and 59 of this *Report*.

Essential oils showing a tendency to *resinify* and to acquire a turpentiny odour are said to keep for an infinite time after adding for each 500 gr. of oil 3 gr. of sodium hydrogen sulphite [2]).

In France, a patent has been granted to Lautier Fils [3]) for a process of manufacturing *pomades* whereby the "châssis" an prepared mechanically for the enfleurage process, *i. e.*, coated with fat and fed with flowers. The latter drop automatically from a hopper on the greased "châssis" which pass the hopper on an endless belt.

H. Schelenz [4]) furnished a small contribution towards the *history of odoriferous and toilet preparations.* Mankind has made use of these articles, more especially of the odorous drugs, from the very beginning. The Bible already mentions these preparations, without, however, giving credit in this respect to the achievements of the ancient Indians, Persians, and Egyptians. In the course of time, one got acquainted with the methods for obtaining the pure odoriferous substances and how to modify the original ways of using them. The scented powders, bags, pomades and sticks were substituted by products of distillation, either the essential oils proper, or to their alcoholic solutions. In the 13th century, for instance, we hear of a "Hungarian Water" rosemary water) which was distilled from the strong-smelling rosemary at first with water, later on with wine. The dispensaries of the Italian, later on also of the French and German monasteries, where the volatile oils were distilled already in the Middle Ages, acquired in the course of time a high standing. In the 18th century, the Carmelites traded an *"Eau des Carmes"* essentially an aqueous distillate of balm (melissa) used for medicinal purposes, and some time after, the Italians made known in Cologne the *Acqua della Regina,* or *"Eau de Cologne".* This preparation is, in Schelenz' opinion, the earliest specimen of an alcoholic solution of essential oils.

Bibliography.

In Ullmann's *"Enzyklopädie der technischen Chemie",* vol. IX (1921), the odoriferous bodies *("Riechstoffe"),* are fully dealt with. The compilers, A. Hesse, A. Ellmer, and R. Haarmann, after giving a short historical introduction (starting from the fundamental

[1]) French. Pat. 521 713, July 3, 1920.. As per *Chem. Zentralbl.* 1921, IV. 1016. — [2]) *The Spatula* 26, 10. As per *Pharm. Zentralh.* 62 (1921), 462. — [3]) French Pat. 524595, Sept. 7, 1921. — [4]) *Seifensieder-Ztg.* 48 (1921), 797.

work .of Tiemann and of Wallach and furnishing a review of the recent development of the technology of the aromatics), deal with the process for preparing odoriferous substances and give furthermore a description of the complex aromatics, their constituents, and how the simple and the complex aromatics are obtained artificially. In the chapter *"Allgemeine Methoden zur Gewinnung der. Riechstoffe"* (General, methods for preparing odoriferous substances), Hesse enters with particular interest into the distillation of otto of rose in Bulgaria, with which process he is acquainted owing to personal inspection. He describes, *inter alia,* a duplex still for distilling roses (illustration) furnished by Egrot, of Paris, which shows some handsome and practical details, just like the most of French machinery, but on the other hand, exhibits several serious drawbacks. Various contrivances, *e. g.*, the badly-constructed still-head, show clearly that the French, unlike the German manufacturers, have not taken the trouble to study from a scientific standpoint the process of the steam-distillation or the water-distillation of plants. — In the chapter dealing with the natural complex odoriferous bodies, the more important essential oils, a well as various aromatics of vegetable or animal origin, their hitherto known components, and the analytical methods serving for the examination of these products are enumerated. — The components of essential oils, insofar as the occur as separate trade articles in the industry of aromatics, have been treated in detail by the authors. For instance, the numerous processes for obtaining vanillin, either from the natural products, or by synthesis, are fully dealt with. — In the last chapter, *"Künstliche Darstellung. einfacher und komplexer Riechstoffe"* (Artificial preparation of simple and composed aromatics), the authors demonstrate, by various instances, how nearly all the ingredients of natural perfumes can be obtained by chemical means. In addition, many works processes for synthesising these products are communicated. A short compilation of statistical figures illustrating the German import and export of essential oils and aromatics during the last decades and showing the rapid evolution of the German *"Riechstoff"* industry prior to the War, forms the last chapter of this treatise which is equally will furnished with illustrations and literary notes.

Towards .the end of the 19th and the beginning of the 20th century, the cultivation of medicinal plants in Germany, as well as in other European countries, such as Holland, had gone down seriously. Since the beginning of the Great War, however more especially in the last years, a change has taken place, to which we referred repeatedly[1]). It was a necessity and an act of material self-respect to cover the demand for medicinal plants from home-grown products. People started again, more especially in Central and Southern Germany, to collect and cultivate drugs on a larger scale. These endeavours were aided by numerous societies, *e. g.*, the "Committee for propagating the collection and cultivation of medicinal and economical plants by Government measures" *(Ausschuß zur staatlichen Förderung der Sammlung und des Anbaus arzneilich, wirtschaftlich und technisch verwertbarer Pflanzen)* at Dresden, the "Hortus-Society" and the "Society for the promotion of the cultivation and collection of medicinal and aromatic plants" *(Gesellschaft zur Förderung des Sammelns und des Anbaus von Gewürz-pflanzen)* in Bavaria, and by the German Pharmaceutical Association *(Deutsche Pharmazeutische Gesellschaft)* of Berlin. However, these endeavours and suffered opposition from various quarters. One of the objections made seemed to be somewhat justified insofar that it was considered unwise to enlarge the area used for drug cultivation in stead of cultivation of victuals and fodder, or of important vegetable raw-materials

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[1]) Cf. *Reports* 1917, 110; 1918, 78.

for industrial purposes. The question arose, is it commendable from an economic standpoint or not to increase the cultivation of medicinal plants in Germany.

Th. Sabalitschka[1]), in an investigation entering very closely into this question, comes to the certain conclusion that in Germany the cultivation of medicinal herbs is in any case a serious necessity which, provided the proper herbs are selected, is particularly provitable for small growers. After dealing with the cultivation of drugs in Antiquity and the Middle Ages, Sabalitschka enters upon the following points: — *a.* consumption in Germany, prior to the War and in future, of drugs obtainable in the country itself; *b.* drug imports into Germany prior to the War; *c.* profitableness (from the producer's view) of drug cultivation; *d.* advantages of cultivating drugs for Germany's trade in general; *e.* directions how to cultivate succesfully medicinal and aromatic herbs in Germany; *f.* cultivation of drugs in states other than Germany, and acknowledgement of the necessity of promoting the cultivation.

Since Sabalitschka's paper touches but lightly our own domain, we content ourselves with the above review. In any case, we recommend sincerely the perusal of this extensive paper which is well supplemented with statistical data on drug imports and exports.

In addition to several short bulletins (in the manner of the Circulars of the Departement of Agriculture, U. S. A.), the Italian "Federazione pro Montibus" has published[2]) a *dictionary* giving the vernacular names of the Italian medicinal and aromatic plants and the corresponding Latin terms.

K. Bournot[3]) gives a *review* for 1920 of the research work on terpenes and essential oils.

Analytical Notes.

K. Hoepner[4]) deals with the various methods *for estimating the alcohol content* in presence of volatile substances. He discusses six methods worked out by the German Alcohol Monopoly Office for determining the free alcohol, not combined with acids, in mixtures of spirit with neutral volatile bodies (perfumes, hair tonics, mouth washs, mixtures of alcohol and esters, with exception of methyl alcohol and of so-called fusel oil) and compares the results with his own experiments. Two of these methods, *a*) diluting and salting out the sample, then distilling and taking the specific gravity of the distillate, *b*) chromic acid process without previous skaking out with sodium sulphate and light petroleum, proved to be unreliable and should be abandoned. Equally the method consisting of diluting with salt solution, then shaking out with light petroleum and distilling the spirit, cannot be recommended. Of the remaining three processes the one consisting of calculating the alcohol content direct from the specific gravity is appliable only in cases when the composition of the preparation is known as to the density and quantity of the dilute alcohol and of the dilute volatile constituent; in addition, a table for calculating the actual alcohol strength must be consulted. The method basing on the process of diluting and shaking out with light petroleum of the neutral volatile ingredients, where the alcohol present is calculated from the density of the distillate, furnishes values which are in the most cases too

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[1]) *Über die Notwendigkeit des Arzneipflanzenanbaus in Deutschland, über seine Rentabilität und seine Vorteile für die deutsche Volkswirtschaft und über die zweckmäßigste Inangriffnahme der Medizinalpflanzenkultur in Deutschland.* Berlin, published by Gebr. Bornträger, 1921. As a copy kindly forwarded to us. — [2]) Domenico Saccardo, *Dizionario dei nomi vulgari delle piante medicinali e da essenze più in uso e dei corrispondenti scientifici latini. Arch. di Farmacognosia e Scienze affini,* vol. 8, 1917. — [3]) *Chem. Ztg.* 45 (1921), 531. — [4]) *Zeitschr. Unters. d. Nahrungs- u. Genußmittel* 41 (1921), 193.

low, anyhow the errors can be eliminated to some extent by certain manipulations. The frequent emulsions occurring here are a great drawback. Satisfactory results are obtained by the following chromic acid process: — dilute with sodium sulphate solution, extract with light petroleum, oxidise the alcohol with potassium bichromate and sulphuric acid to acetic acid, calculate the alcohol present from the amount of bichromate consumed — but only if the portions of water-soluble esters remaining in the sulphate solution are duly taken in consideration, as well as the increase in volume caused by solution of the volatile components. For carrying out this bichromate process, small quantities, say 5 ccm., are sufficient.

The author finally gives the following improved directions for estimating the alcohol contained in alcoholic preparations together with volatile substances a) by means of the specific gravity, b) by the chromic acid process: —

a) 50 gr. of the sample, which must be free from glycerin, resins, or other extract substances, are given into a separating funnel, 50 gr. water then added, finally 50 cc. light petroleum ("petroleum benzine") and shaken vigorously several times. The next day, the lower layer is given into a tared flask and brought to 99 gr. The alcohol content as calculated from the density must be multiplied by 2. Special directions are given for removing glycerin, resin, or free acids before carrying ont the estimation, in case these bodies should be present.

b) 25 or 50 cc. of the sample (according to the preliminary alcohol content as calculated from the density) are given into a tared flask containing about 25 cc. of water, then weighed and diluted up to 500 cc. with a 12.5 per cent. solution of sodium sulphate. The mixture is shaken repeatedly and vigorously with petroleum benzine, the sulphate solution drawn off when fully clear and shaken with fresh 50 cc. petroleum benzine. The next day. 10 cc. of the fully clear sulphate solution are mixed with 25 ccm. 2N-potassium bichromate solution and 50 cc. dilute sulphuric acid and cooled down under the tap. After a lapse of two or three hours, the mixture is transferred into a 500 cc. measuring flask and water is added up to the mark. Of this solution, 50 cc. are mixed with 20 cc. potassium iodide solution, then diluted, after 10 to 15 minutes with about 100 cc. water and titrated balk with decinormal sodium hyposulphite solution, using starch solution as indicator. — In order to ascertain whether the sodium sulphate solution used for the oxidation still contains a small amount of water-soluble esters, 200 cc. of the sulphate solution are mixed with 10 cc. standard alkali solution, and the next day the amount of alkali not required for saponifying the esters possibly present is titrated back with standard acid. An amount of 0.2 cc. alkali is not considered. — Glycerin, resins, free acids or bases are removed before carrying out the examination, as stated above. — Each cc. decinormal bichromate or hyposulphite solution = 0.0011512 gr. alcohol.

W. Olczewski[1]) gives the following directions for estimating the alcohol content in essences: — 25 gr. of the liquid under examination, 25 gr. saturated salt solution, and 20 gr. petroleum ether (b. p. not exceeding 60°) are given into a separating funnel, shaken thoroughly and as soon as the liquid is clear the lower layer is drawn off into a 300 cc. flask. The residual petroleum ether is shaken once more with 15 cc. salt solution, the aqueous layer is given into the flask and the contents, after adding some magnesium carbonate and débris of porous plate, are distilled into a pyknometer of 50 cc. capacity.

When liquids show a strong tendency to emulsify with petroleum ether, or are rich in essential oil, double distillation is resorted to. From 25 gr. of the preparation and 50 gr. water, with addition of some alkali about 50 cc. are distilled (in case of foaming, the alkali is omitted, and tannin is added) directly into a separating funnel, the distillate is saturated with salt, then shaken out with 25 cc. petroleum ether, drawn off into a 300 cc. flask (the petroleum ether is likewise shaken out once again with salt solution), and the united aqueous liquids are again distilled, as in the first-mentioned process, into a pyknometer of 50 cc. capacity.

The methods published hitherto for the detection of alcohol in essential oils are discussed by Utz[2]). We abstain from mentioning them here, since the author likewise has found them to be more or less unreliable. The process described in Gildemeister's

[1]) Pharm. Zentralh. 62 (1921), 288. — [2]) Deutsche Parf. Ztg. 7 (1921), 217.

text-book[1]) serves best for qualitative tests (formation of iodoform) and for approximate quantitative determinations (shaking out a fairly large portion with water or salt solution).

The process devised by Verley and Boelsing[2]) for the quantitative *estimation of alcohols and phenols* (more especially of santalol, menthol, and eugenol) has been re-examined by H. W. van Urk[3]). The result was this that none of the substances mentioned above can be estimated accurately by that method. Since years ago we entered fully into the details of the process and found it to be unreliable[4]) we consider it unnecessary to occupy ourselves furthermore with van Urk's publication.

In order to *determine the amount of phenols* in essential oils the method devised first by Gildemeister[5]) for testing thyme oil and improved later on by us[6]) has, in general, proved satisfactory; it consists in shaking 10 cc. oil in a cassia flask of fully 100 cc. capacity with a caustic soda solution of 3 or 5 per cent., and calculating the phenol content from the amount of the oil dissolved in the lye. W. H. Simmons[7]) proved by way of experiment, that with thyme and cinnamon leaf oils 5 cc. oil on treatment with a 5 per cent. caustic potash lye, give a distinctly higher proportion of phenols than when 10 cc. of the oils are employed. Hitherto, the author was unable to prove with certainty whether the lower or the higher values were the correct ones. Comparative tests with clove, bay, and pimento oils gave the same results with 5 or 10 cc. oil. (On the whole, too strong lyes give too high results, since the lye, in connection with the phenol alkali, dissolves also part of the non-phenols. For this reason, we shake some oils, e. g., clove oil, with a caustic solution of but 3 per cent.)

With the object to determine the composition of mixtures of eugenol and *iso*-eugenol, in the preparation of vanillin from eugenol, P. V. McKie[8]) constructed a curve illustrating the melting points of mixtures of pure eugenol and pure *iso*eugenol benzoates, m. p. 69.5 and 104° respectively, following the method described in a previous paper[9]). A well-marked eutectic point was observed at a temperature of 56.5°, corresponding with a composition of 25.5 per cent. of *iso*eugenol benzoate. Although at temperatures from 83 to 86°, and at compositions approximating to the equimolar mixture, the curve showed a discontinuity, the use of the melting point as a means of determining the composition of mixtures is thereby not invalidated.

The authoress obtained the esters by dissolving the crude oil, resulting from the isomerisation of eugenol, in pyridine, and treating with some 25 per cent. excess of benzoyl chloride. The major portion of the benzoates separates as a solid, and a further quantity on pouring the pyridine solution into dilute sulphuric acid. The resulting benzoates were dissolved in ether, from which, on evaporation of the ether, the solid benzoate mixture is obtained.

When, years ago[10]), we *estimated citronellol* according to the formylation method, we found that part of the alcohol undergoes a change. In order to elucidate this reaction, A. St. Pfau[11]) formylated each 100 gr. of citronellol (b. p. 105° [7.5 mm.], 6 months' old preparation) by boiling for one hour with each 200 cc. of 100 per cent. and of 85 per cent. formic acid. The formylation products (ester v. 295.4 = 96.4 per cent.,

[1]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 612. — [2]) Cf. *Report* April 1902, 25. — [3]) *Pharm. Weekblad* 58 (1921), 1265. As per *Chem. Zentralbl.* 1921, IV. 1145. — [4]) Cf. *Report* April 1903, 27. — [5]) Hager, Fischer and Hartwich, *Kommentar zum Arzneibuch f. d. Deutsche Reich, 3. Ausg.* Berlin 1892, 1st ed., vol. I, p. 377. — [6]) *Report* April 1907, 119. — [7]) *Perfum. Record* 12 (1921), 394. — [8]) *Journ. chem. Soc.* 119 (1921), 777. — [9]) *Ibid.* 111 (1918), 799. — [10]) Cf. *Report* October 1913, 64. — [11]) *Journ. f. prakt. Chem. N. F.* 102 (1921), 276.

and 263.0 = 84.3 per cent. citronellol) were separated into 6 and 5 fractions respectively. It was then found that there had been formed on the average, in formylation:—

	With the 100 per cent. acid	With the 85 per cent. acid
Terpenes and citronellol	1 per cent.	3 per cent.
Citronellyl formate	20 „ „	30 „ „
Citronellyl glycol monoformiate[1]	35 „ „	40 „ „
Citronellyl glycol diformiate[2] .	29 „ „	12 „ „
Residue, polymerized	15 „ „	15 „ „

By the same treatment, citronellyl formate gave rise to a product of the following composition:—Unchanged citronellyl formate, 35 per cent.; citronellyl glycol diformiate, 50 per cent.; polymerized residue, 15 per cent.

Hence the exceedingly high values obtained by determining pure citronellol by the formylation method[3]), are due to the formation of citronellyl glycol diformiate.

Pfau concludes, as result of his work, that the formylation process for estimating citronellol furnishes irregular values and affords no clue as to the true content of citronellol. This is nothing novel, as we always have pointed out[4]) that this process is not an exact one, although it may be satisfactory in practical work.

Equally, C. T. Bennett[5]) tested the formylation method by varying the conditions and came to the conclusion that the method is unreliable for the determination either of citronellol or citronellal.

With regard to these two articles by Pfau and Bennett, W. H. Simmons[6]) is of opinion that both workers confirm his own conclusions on the subject, but apparently ignore what he considered to be most important, viz., that the method is a very useful one for comparing the relative proportions of citronellol in different geranium oils, as was suggested by him in 1913. Subsequent experience with a very large number of samples of African and Bourbon geranium oils fully confirmed the view which Simmons then expressed. It is very important to adhere strictly to one and the same direction and to heat for exactly 60 minutes on a boiling water bath, and not on a sand bath.

For the *estimation of terpin hydrate* in elixir of terpin hydrate Nat. Form.[7]), A. G. Murray[8]) gives the following directions:—The elixir is mixed with a solution of 20 gr. common salt in 100 ccm. of water until the alcohol content is from 10 to 15 per cent. by volume. The mixture is shaken out with four portions, one-fourth volume each, of chloroform containing 5 to 7 per cent. by volume alcohol. Each portion of the solvent is washed successively with 5 ccm. salt solution, then filtered into a tared beaker, and evaporated by aid of a blast, avoiding application of heat. (On evaporating an alcoholic solution of terpin on the water bath, about 10 per cent. of the terpin hydrate were found to volatilize.) The residual pure terpin hydrate is dried at the open air and then weighed. The error was only + 0.8 per cent.

The acetylation of both hydroxyl groups in terpin may be carried out by boiling the glycol for three hours with eight times its weight of acetic acid and five times its weight

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[1]) d_{15^0} 0.9651; $\alpha_D + 1^\circ 46'$; n_{D15^0} 1.4488. — [2]) d_{15^0} 0.9976; $\alpha_D + 1^\circ 33'$; n_{D15^0} 1.4425. — [3]) Cf. *Report* October 1913, 64. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 600. — [5]) *Perfum. Record* 12 (1921), 351. — [6]) *Ibidem* 398. — [7]) It contains, in addition to about 1 grain (0.175 gr.) of terpin hydrate, tincture of sweet orange peel, spirit of bitter almond, alcohol, glycerin, and syrup in 1 fl. dr. — [8]) *Journ. Amer. pharm. Ass.* 10 (1921), 440.

of a neutral solvent, *e. g.*, turpentine oil, with addition of sodium acetate. Basing on this reaction O. Fernandez and N. Luengo[1]) worked out a method for the estimation of terpin.

Although the inaccuracy of the phosphoric acid process for the *determination of cineole* is long known — even C. E. Sage and J. D. Kettle[2]) admit readily that the method is not so exact as a purely chemical method — we very frequently meet with endeavours to puff up that process whenever an opportunity arises. Such an opportunity arose recently with the publication of Tusting Cocking's cresineol method[3]) and Kleber's and von Rechenberg's[4]) solidification point test. Sage and Kettle point out that the former author[5]), when comparing the "phosphoric" and "resorcinol" methods, found considerable discrepancy between the results of both methods (which fact we take as proof for the inaccuracy of the "phosphoric" method), and now they publish the results of comparative cineole determinations in a few eucalyptus oils and cineole samples, carried out according to the "phosphoric", cresineol, and solidification point methods. The results which differ to the utmost by 6 per cent. and are hardly worth any discussion, are, in our opinion, not in favour of the phosphoric acid process, as the authors maintain.
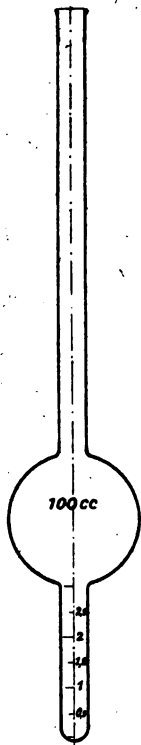
F. B. Power[6]) recommends the following process for *detecting methyl anthranilate* in fruit juices:—From 500 ccm. of the liquid 200 ccm. are distilled off, and the distillate which in presence of an appreciable quantity of the ester shows a bluish fluorescence, is shaken out three times with each 10 ccm. of chloroform (*not* ether). The residue obtained on careful evaporation of the chloroform extract is immediately treated with 2 ccm. of 10 per cent. sulphuric acid, the acid liquor is transferred to a test-tube and cooled. To the liquor one drop of a 5 per cent. solution of sodium nitrite is added, then a few crystals of urea, and subsequently one of the following two reagents:— *a.* a mixture of one ccm. of a 0.5 per cent. solution of pure β-naphthol containing 0.2 per cent. of sodium hydroxide, one ccm. of a 10 per cent. solution of sodium hydroxide, and one ccm. of a 10 per cent. solution of monohydrated sodium carbonate, $Na_2CO_3 \cdot H_2O$. If not less than 0.0001 gr. of methyl anthranilate is present, a yellowish-red precipitate will be produced; *b.* one drop of dimethylaniline, and, when the latter has completely dissolved, a slight excess of a 10 per cent. solution of sodium hydroxide. The yellowish coloration produced in presence of not less than 0.001 gr. of the ester changes to red on slightly acidifying the mixture with dilute sulphuric acid.

By this process the author believes to have overcome the errors such as possible with the Erdmann method[7]) (incomplete separation of the ester which is not free from foreign admixtures). The results of the investigation of grape juices by this process are reserved for a future communication.

The *estimation of phenylacetaldehyde* in the cassia flask according to the bisulphite method is often connected with difficulties and is frequently inexact, since the heavy non-aldehydic (polymerized) constituents of the aldehyde remain at the bottom of the flask. A. Reclaire[8]) recommends to modify the process as follows:—

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[1]) *Ann. soc. española Fis. Quim.* [2] 18 (1920), 158. As per *Chem. Zentralbl.* 1921, IV. 687. — [2]) *Perfum. Record* 12 (1921), 44. — [3]) Cf. *Bericht* (German) 1921, 65. — [4]) *Ibidem* 35. — [5]) Cf. *Report* October 1910, 67. — [6]) *Journ. Amer. chem. Soc.* 43 (1921), 377. — [7]) *Berl. Ber.* 35 (1902), 24 and 2355. — [8]) *Perfum. Record* 12 (1921), 341.

5 ccm. of phenylacetaldehyde are introduced into a 100 ccm. flask of special construction, then 20 to 25 ccm. of solution of sodium bisulphite (containing about 30 per cent. $NaHSO_3$); the mixture is shaken vigorously for some minutes, and the whole is placed in a water-bath. After some time, boiling water is gradually added until the solid compound at first produced is completely dissolved. More water is then added, and the non-aldehydes settle down in the graduated tube, where the volume can be read off when cold.

As to the *identification of nitrobenzene* when present in bitter almond oil, see p. 6 of this *Report*.

Re the *estimation of vanillin* according to Doherty see p. 100 of this *Report*.

Physical Notes.

As is generally known, the reason why the vapour tension curves of two substances do not run parallel to each other is to be found in the différence of the changes of tension with identical changes of the temperature. The numerous curves compiled by C. von Rechenberg[1] show that about 2000 pairs of curves cross each other. When, in agreement with v. Rechenberg, the liquid and solid states are considered as chemical formations which on heating are decomposed into vapour molecules, then the different stability of the molecular complexes is the cause of the varying evolution of vapour, hence the latter is a measure for the former. When working out the entire material v. Rechenberg was able to classify all the substances investigated in relation to the increase in vapour pressure for the equal rise in temperature, and this classification was clearly in accord with Rothmund's[2] solubility series. It may, therefore, be concluded that in both cases the regularity is a result of the identical cause mentioned above.

Furthermore, C. von Rechenberg[3] utilized his excellent material of vapour tension curves for testing Bancroft's rule which implies that all mutually soluble liquids of which the vapour tension curves cross each other form "distinguished" mixtures with either a minimum or maximum boiling point. v. Rechenberg was able to confirm the general applicability of that rule, but with the restriction that such mixtures with "distinguished" boiling points are limited to a certain range of pressure.

With the object to investigate in the laboratory the separation of binary mixtures by continuous distillation, A. F. Dufton[4] constructed a continuous still with a still-head as had been devised by S. F. Dufton[5]. The mixture to be separated was fed from a small flask, where it was electrically pre-heated to its boiling point, into the middle of the column. A siphon kept the level in the preheater constant. The lower part of the still was also heated electrically by a wire coil and the current required was measured by a watt-meter. To obviate any loss of heat from the lower part of the column, a thick lagging of cotton-wool surrounded by a steam-jacket was employed. Exact thermometers at the top of the still-head and at the bottom of the column indicated the purity of the separating products.

Starting from a 50 per cent. mixture of benzene and toluene the author succeeded in regulating the still to work automatically, yielding pure benzene and pure toluene continuously. By measuring the head supply it was found that the separation of one

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[1] *Zeitschr. f. physik. Chem.* 99 (1921), 87. — [2] *Ibidem* 26 (1898), 489. — [3] *Ibidem* 99 (1921), 105. — *Journ. chem. Soc.* 119 (1921), 1988. — [5] *Journ. Soc. chem. Industry* 38 (1919), 38 T; *Bericht* (German) 1920, 101.

gram of benzene required 1340 calories. As the theoretical quantity of heat required is calculated to be 208 calories[1]) the thermal efficiency of the still was 15.5 per cent.

When other still-heads were employed, for instance copper gauze discs, or thin-walled cylindrical glass beads 4 mm. long and 4 mm. in diameter, the thermal efficiency[2]), with a 50 per cent. mixture of both hydrocarbons, was up to 47 per cent.

L. Smith[3]) publishes some laboratory notes on the efficiency of still-heads in vacuum distillation. We agree with the author that the circumstances, in vacuum distillation, are not fully comparable to those under atmospheric pressure; in the present case, however, the method employed for testing was not sufficiently sensitive, so that the values derived afforded no evidence towards the question which has been elaborately studied by other authors[4]).

Years ago it has been demonstrated by A. Hantzsch[5]) that it is possible to test the constitution as well as the *purity of terpenes* by means of the *ultraviolet ray absorption*. A. Müller[6]) employed this method for examining citronellol, geraniol, and their derivatives. As the author communicates, it is sufficient, it is true, for obtaining the pure alcohols and their acetates to make use of the ordinary distillation process, whereas the purification of the cyclic alcohols and their esters is said to be difficult. Unfortunately though, he furnishes but insufficiently the constants of the preparations under examination (the refractive index being nowhere recorded, and the optical rotation only in part) from which the purity of the preparations might have been judged. The solutions were prepared by means of optically pure alcohol. A citronellol obtained from Java citronella oil (b. p. 112.5 at 8 mm., d_{150} 0.8612, α_{D200} 2° 16'[7]) showed stronger absorption than a citronellol obtained from citronellal by reduction (b. p. 113.2° at 8 mm., d_{150} 0,8600, α_{D200} 4° 5'). A sample of geraniol (b. p. 108.2° at 9 mm., d_{150} 0,8836) purified from its calcium chloride compound[8]) showed a still lower absorption, and that of reuniol lay between that of citronellol and geraniol, but nearer towards the latter. With the acetates of the two alcohols the distance of the absorption curves was even larger. With the cyclic alcohols (cyclisation was performed by treating the esters with phosphoric acid at low temperature) the absorption bands approached each other the closer, the more the esters were subjected to fractional distillation. The purest preparations, *cyclo*-citronellol (b. p. 97 to 101° at 8½ mm., d_{150} 0.9023, α_{D200} 2° 30'[7]) and *cyclo*-geraniol (b. p. 96 to 98° at 11 mm., d_{150} 0.9462) showed but a feeble difference in the position of the absorption bands; with the cyclic esters, however, the differences were greater. The hydrogenated alcohols: — dihydrocitronellol (b. p. 113.5° at 15 mm., d_{150} 0.8565) and tetrahydrogeraniol (b. p. 116 to 117.5° at 14.5 mm., d_{150} 0.8621), with which the bands were located more towards the ultraviolet part of the spectrum, possessed nearly the identical absorption. Since likewise the results of the chemical examination indicated that in the hydrogenated alcohols the alkyl group occupied the same position, the alcohols proved to be *2 : 6-dimethyl octanol-8*.

With regard to earlier chemical investigation[9]), the author, basing on his optical examination, arrives at the conclusion that reuniol is merely a mixture of citronellol

[1]) *Journ. Soc. chem. Industry* 38 (1919), 38 T; *Bericht* (German) 1920, 101. — [2]) *Phil. Mag.* VI, 42 (1919), 633. — [3]) *Journ. f. prakt. Chem.* II, 102 (1921), 295. — [4]) Cf. *Bericht* (German) 1920, 101. — [5]) Cf. *Report* April 1912, 156. — [6]) *Berl. Berichte* 54 (1921), 1466. — [7]) The direction of the rotation is not stated. — [8]) In a paper published in the *Deutsche Parfümeriezeitung* dealing with the identical subject the author believes this calcium chloride compound to have been discovered in our laboratory. This is a mistake. This compound was first obtained by O. Jacobsen (*Liebig's Ann.* 157 [1871], 234. — [9]) Cf. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 364. *Report* October 1904, 119.

and geraniol (with at least 60 per cent. of geraniol), and that it must be struck off from chemical literature.

The absorption power of ultraviolet rays by various phenols and phenol ethers has been studied by Th. H. Durrans[1]. *Iso*eugenol proved to absorb ultraviolet rays much more than eugenol, and by methylating a phenol hydroxyl, *e. g.*, in *iso*eugenol, the absorption power for ultraviolet light is doubled. The absorption is likewise raised, in a still higher degree, by introducing the allyl side-chain, whereas by the propenyl side-chain the power of absorbing ultraviolet light becomes very small, as was shown by comparison of anisole, anethole, and methyl chavicol.

The investigation started by Rupe on the *influence of the constitution on the optical rotation* of active substances has been continued by A. Krethlow and K. Langbein[2]. In order to obtain further insight into the relation between rotatory dispersion and spectral absorption the authors examined such optically active substances as show marked or at least incipient, selective absorption of light in the neighbourhood of the visible spectrum as to their abnormal rotatory dispersion. Of 19 optically active bodies examined, six were perfectly normal in their optical behaviour, as they showed neither abnormal rotatory dispersion nor any selective absorption of light (amongst then camphorylidene-*3*-acetic acid methyl ester and camphoryl-*3*-acetic acid). Seven substances manifested anomalies in rotatory dispersion, amongst which were various menthyl esters, *e. g.*, of diacetoacetic and of pyruvic acids. Benzalcamphorylidene acetone and styrylbenzoylacetic acid menthyl ester behaved polarimetrically normal, but showed beginning spectral absorption.

The authors deduct from their investigations that a parallelism between abnormal rotatory dispersion and selective spectral absorption does not appear to exist. Amongst 33 bodies, only three (the white diphenylmethylacetoacetic and phenylbenzoylacetic acid menthyl esters, besides the pale yellow diphenylmethylal camphor) were found which showed both anomality in the rotatory dispersion and selective absorption of light[3]).

F. Eisenlohr[4] reports on the molecular refraction of higher-melting bodies, and how the corresponding refractive indices are recalculated on the standard temperature of 20°.

A. Müller[5] observed *anisotropism* in the melting point of dianisal*cyclo*hexanone (prepared from pure *cyclo*hexanone and anisic aldehyde). At 160 to 161°, the body liquefied into an opaque mass which clarified suddenly at 171°. The phenomenon of voluntary spreading-out on water in a very thin film (long known with oleic acid and other bodies) has been observed by A. Marcelin[6] with a series of other substances. The experiments were carried out in the following manner: — When a small piece of camphor is floated on water, the surface of which was sprinkled with talc powder, one could observe how the talc grains were driven away from the camphor piece so that an empty circle was formed round the latter. The diameter of this "halo" reached a maximum depending upon the equilibrium ruling between the velocity of the dissolving of the thin camphor layer formed, and of the re-formation from the camphor piece. A series of photographs of this process was taken. From the area of the circle and the loss in weight of the camphor piece the thickness of the layer was calculated. Solid benzene (below 3° C.) showed the same phenomenon when floating on water.

[1]) *Perfum. Record* 12 (1921), 370. — [2]) *Liebig's Ann.* 423 (1921), 324. — [3]) Cf. *Report* 1918, 96. — [4]) *Berl. Ber.* 54 (1921), 2857. — [5]) *Ibidem* 1481. — [6]) *Compt. rend.* 173 (1921), 79.

When repeating the experiment with water on which oleic acid had been spread out previously, a halo was likewise formed, the diameter of which allowed of comparing the relative surface tension. Hereby the following figures resulted: — dimethylpyrolidone, 31.5; dimethylcampholic acid amide, 29.7; isobutylborneol (-camphol), 20,4; menthol, 20.4; p-toluidine, 16.7; camphor, 13; thymol, 12.1; borneol, 11.1; propylcamphocarbonic acid methyl ester, 9.4; benzal camphor, 0.94.

According to F. Hogewind[1]), nearly all odoriferous bodies, after long standing of their aqueous solution, show *colloid properties*. The odour was then found to be but slightly less intense than with the original oil; in addition, a layer of pure water, when poured carefully on such a colloidal solution, was found to assume the odour of the aromatic in question. These phenomena are readily explained by the well-known fact that the bodies mentioned show more or less the tendency to polymerise and resinify partly. In this process products are always formed which are far less soluble, and which, owing to the low concentration of the initial solutions, yield stable hydrosols.

A. Müller[2]) describes and recommends an apparatus for determining the *viscosity* of essential oils termed "viscosostalagmometer". As years ago[3]) we established by way of experiment that the determination of this constant is of but little value when judging essential oils, we need not enter into a description of Müller's apparatus, which in its main features differs but slightly from the viscosimeters devised by Arrhenius, Ubbelohde, Engler, and others.

Botanical Notes.

Two *hybrids of spike and lavender* are described by M. Humbert[4]).

Hybrid A, growing up to 1 m. height, resembles in general habit and appearance a strong *L. latifolia* and is found here and there, more or less isolated, in the north of St. Saturnin-les-Apt at about 800 m. altitude, also near Buis-les-Baronnies about 400 m. altitude, in the Nyonais, and in the Causses. The flower stalks, divergent as in *L. latifolia*, generally bear in the axils of two higher leaves a pair of secondary flowering branches. At the base of the bushy, more or less interrupted inflorescences, often exceeding 10 cm. in length, the pairs of lower leaves form false rosettes. The bracts, in whose axils 6 to 12 flowers stand, remain green a long time even after flowering, at least in their upper part.

Hybrid B, whose height varies between 30 and 80 cm., resembles more *L. officinalis*, is found in great abundance throughout the entire zone of contact between *L. latifolia* and *L. officinalis*, often as numerous as the parents. The flower stalks are more or less divergent, generally simple, but sometimes bear in the axils of two higher leaves a pair of secondary branches. The lower leaves, approaching the base of the flower-bearing branches, form false rosettes but not so distinct as in *L. latifolia* or in hybrid A. The bracts are brown and membraneous after flowering. The slender inflorescence is 1.5 to 6 cm. long, usually not interrupted; 1 to 5 flowers stand in the axil of each bract.

The following characters are common to both hybrids: — 1. The flowering begins later than in *L. officinalis* and earlier than in *L. latifolia*. 2. The seeds are almost always sterile. 3. On bruising the plant a camphoraceous odour is noticed.

[1]) *Archives néerland. de Physiol. de l'homme et des animaux* 5 (1920), 153. — [2]) *Chem.-Ztg.* 45 (1921), 759. — [3]) Cf. *Report* April 1901, 31. — [4]) *Perfum. Record* 12 (1921), 177.

Two other hybrids, A' and B', from *L. officinalis var. pyrenaica* and *L. latifolia*, correspond to the hybrids A and B described above. The species B'[1]) resembling more *L. pyrenaica* and termed *L. aurigenara*[2]) differs from hybrid B by the large size of its bracts. The more frequent hybrid A' shows greatly developed bracteoles and an odour of camphor. Side by side with those hybrids there exist various other hybrid forms.

R. Laubert[3]) gives a description of the most important *diseases of aromatic plants*, their origin and symptoms. Amongst the diseases known to occur with roses[4]), the much-dreaded white rose-blight takes the foremost place. It is caused by a fungus belonging to the *Erysibaceæ, Sphærotheca pannosa*, (Wallr.) Lev. f. *rosæ*, and appears in shape of a white, dust- or flour-like deposit on the leaves, particularly on the tops of the young shoots. On the petioles and the calyces of the blossoms as well as on the fruits the white fur shows a coarse, fluffy appearance. Some rose varieties are attacked by this fungus but slightly, others are known to be very ready victims, *e. g.*, the Crimson Rambler. — Another rose fungus, *Phragmidium subcorticosum,* (Schrank) Winter (N. O. *Pucciniaceæ*) is recognized by its bright orange-red, oblong or round, pulvinate weals occurring in spring on the leaves, their stalks, and on other green parts. In the course of the summer, there may be found on the back side of the leaves small, light orange-yellow dusty pustules, at first only a few, but growing in number, which then turn black and sooty; on the upper side of the leaf, corresponding small yellow or reddish spots appear. Since the leaves attacked by this fungus turn yellow and fall off prematurely, the plants are seriously injured by this disease. The most of the high-class varieties known as remontant roses are readily attacked, in a less degree the tea hybrids and tea roses, whereas climbing and mountain roses are hardly ever afflicted. — The disease known as black spot blight *(Sternrusstau)* of the rose leaves occurs principally during damp weather and manifests itself on the upper side of the leaves in shape of round brownish-black or violet-black spots which on magnification prove to be composed of small dots and show a finely-radiated, fringed margin. The disease which likewise causes the leaves to fall off prematurely is generated by a fungus sponging upon the green leaves, *Actinonema rosæ*, (Lib.) Fries (N. O. *Sphaerioidaceæ*). Low-growing roses are preferably attacked by this disease. — The *Peronospora* disease of the roses is, on the whole, not very common, but at times rather dangerous. It can be recognized by small spots on the leaves, which occur irregularly and sporadically and are in the beginning yellowish-grey, later on yellowish-brown. The disease occurs sometimes with roses cultivated under glass and with rose seedlings and is caused by the sponging fungus *Peronospora sparsa*, Berk. (N. O. *Peronosporaceæ*). Some rose gardeners consider the disease caused by a fungus named *Coniothyrum Wernsdorffiæ* Laubert[5]) (brown blight) to be the most dangerous of all rose diseases, since at times much damage is caused by this fungus. Early in spring, sporadic big round dark spots get visible on the green bark of the branches, particularly on the buds, which afterwards turn leather-brown to greyish-brown. Later on, the mortified bark splits up and peels off, whereby the woody interior gets visible. When the spot

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[1]) As per a paper by J. Gattefossé (*Parfum. moderne* 14 [1921], 207) this hybrid was found in 1877 in the enees by Father Sennen and was termed *L. Senneni* by Abbé Coste. The hybrid *L. aurigerana*, Mailho, on other hand, shows more the character of *L. latifolia* and would correspond to the hybrid A. — [2]) In the idex Kewensis, a species *L. aurigerana*, Mailho is enumerated. — [3]) *Deutsche Parf. Ztg.* 8 (1922), 1, 17. — Cf. *Report* October 1915, 71. — [5]) The so-called *Carcinoma rosæ*, recognizable by the abnormal exuberances, generated not by the fungus *Coniothyrum Fuckelii*, but by lesions and action of the frost early in March. ie fungus is but a secondary phenomenon. Cf. Sorauer, *Handbuch der Pflanzenkrankheiten*, 1921, vol. I. p. 658.

spreads round the branch the latter mortifies partly or totally. — The so-called *Botrytis* rot of the rose buds occurs in the summer when in the flowering time the weather is cool and damp. The rose buds, instead of opening, do not develop further, change colour and get covered with an ash-grey coating of the fungus *Botrytis cinerea,* Pers. (N. O. *Mucedinaceæ.*) Under favourable growing-conditions the plant is, in the most cases, not liable to suffer seriously by this fungus.

For combating these rose diseases the author recommends partly spraying with sulphurated substances, *e. g.,* powdered sulphur, solutions of calcium or potassium sulphide, &c., in case of *Sphaerotheca pannosa,* partly prophylactic treatment with sprays of copper preparations (copper-and-lime solution against *Phragmidium, Actinonema, Peronosposa* and other leaf fungi). Careful treatment of the roses, such as proper cutting and pruning, correct fertilization and tilling of the beds is likewise most essential.

About 35 different fungi have been found on the various species of mint, but only a part of them are parasites or cause diseases. Of the noxious fungi, the following may be mentioned. *Puccinia Menthæ,* Pers. (N. O. *Pucciniaceæ*), the very common mint rust, occurs in two chief forms, the uredo- or summer-spores, and the teleuto- or winter-spores. In summer time cinnamon-brown, wart-like, dusty pustules appear on the back side of the leaves, at first sporadically, afterwards in growing numbers, which constitute the stroma generating the unicellular summer (uredo) spores with pale yellow, short-bristled membrane. The uredospores communicate the disease in summer from leaf to leaf and from plant to plant. In addition to the brown pustules, largar black dust-like tubercles appear, the teleuto-stroma of the same fungus. They generate the oval, bicellular winter spores with a brown, wart-like membrane and long colourless petioles. When these teleutospores germinate in the next spring and form sporidia which infect the mint, the second, less common form of the disease develops in which the stalks and the petioles of the leaves acquire abnormal stoutness and are streaked by the mycelium of the rust fungus. The mint rust which occasionally causes deterioration of the odour of the plant and its oil, and often enough has destroyed the entire crop, is found not only on numerous species of *Mentha,* but also on various other members of the family *Labiatæ (e. g., Calamintha, Clinopodium, Origanum, Satureia).* However, not all the species an infected equally often or in an equal degree. For instance, *Mentha arvensis* is attacked by one of the eight different varieties of *Puccinia Menthæ* which does not or but slightly attack other species of *Mentha.* These biological properties must be considered when combating the rust disease. By raising the mint plantations in suitable uninfected soil the appearing of the disease can be warded off or at least its spreading can be limited.

Another disease, the so-called mint mildew, has been observed occasionally on *Mentha arvensis.* The green parts of the plants get covered with a white, flour-like coating which originates from an *Erysibacea, Erysiphe Galeopsidis,* D. C., or *E. Cichoracearum,* D. C. — The fungus *Septoria Menthæ,* (Thurm) Oud. causes the septoria spotted-leaf-disease of the mints which appears on the leaves of *Mentha arvensis* and perhaps also of other species in shape of black-lined, dark, later on light-grey spots. The mint septoria seems to be of minor importance. The same holds good for the following three diseases: — The ramularia spotted-leaf-disease (caused by *Ramularia menthicola,* Sacc. *[Mucedinaceæ]*) on the leaves of *M. silvestris, M. aquatica, M. canadensis, M. arvensis;* the physoderma weal disease of mints (caused by *Physoderma Menthæ,* Schroet. *[Cladochytriaceæ]* and characterized by blackish-brown callosities on the stalks and leaves of *Mentha aquatica*), and the synchytrium papillary disease of mints (caused by *Synchytrium aureum,* Schroet. *[Synchytriaceæ]*), golden-yellow nodules on the stalks and

leaves of *Mentha aquatica*. The fusarium stalk rot, caused by the mycelium of *Fusarium Dianthi*, Prid et Del. and *F. roseum*, Meng. *(Tuberculariaceæ)*, which occurs occasionally in mint plantations is not quite as harmless as the preceding fungi. In this disease, the stalks turn blackish-brown at the base and wither. The following measures are recommended against this disease: — Destroying of all infected plants, suspending the cultivation of mints for several years, and, if necessary, disinfecting the soil.

Phytophysiological Notes.

With the object of studying the *process of formation*, in the plant, *of the essential oil*, J. Politis[1]) investigated the secretory hairs of various labiatæ and geraniaceæ. In the secretory cells of the hairs, during the first stage of their formation, numerous oblong and twisted "chondriocontes"[2]) are observable which contain a tannin compound. These "chondriocontes" widen gradually at each of their ends and separate thus that both from each a separate globule. These globules increase in size and pass over into the vacuoles of the cell where in course of time they are dissolved by the vacuole liquid. The content of the vacuole then shows feeble refractory power, and instead of the disappearing tannin, essential oil is formed[3]).

E. Canals[4]) investigated the influence exercised by *rays of varying wave-lengths* on the *formation of essential oil* in the plant. For this reason, the author transplanted young thyme plants grown in uncultivated land into pots and arranged them in boxes beneath ordinary (1), blue (2), or red (3) glass panes. After lapse of 20 days, all the plants in box (1) were in bloom, but showed pale blossoms, long stalks, and light green leaves. The plants in box (2) were like the former, some of them had faded away. In box (3), but a very few plants had attained a poorly blossoming stage, their stalks were excessive long and the leaves very broad. The thyme plants had entirely lost their xerophilous character. The oils distilled from the various plants showed the following percentage of thymol: —

> Plants in box 3 (red glass) . . . 25.5 per cent. thymol
> „ „ „ 2 (blue glass) . . . 36 „ „ „
> „ „ „ 1 (ordinary glass) . 45 „ „ „
> „ from open air . . . . . 52 „ „ „

From these observations the author concludes that the thymol content of the oil decreases to the same extent as the plant loses its xerophilous character, and that the chemically active blue rays exercise an unfavourable influence on the formation of thymol which is far more marked with the calorific red rays.

The result of this study is in accord with earlier investigations and might have been expected. According to Lubimenko and Novikoff[5]), light is indispensable in the formation of essential oil in the plant, but increased etiolation, at least within certain limits, raises the yield of oil. On the other hand[6]), in most cases the rays of high

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[1]) *Compt. rend.* 173 (1921), 98. — [2]) The term "chondriocontes" is a newly-created one and is not to be found in the literature at our disposal. With "chondres" various species of granules are designed which occur in the nucleus and form the connections between the *linæ* in the frame. — [3]) Already years ago, various scientists, *e. g.* Heckel and Schlagdenhauffen (*Compt. rend.* 114 [1892], 1291) favoured the theory that there exists some connection between the formation of essential oil in the plant and the tannins. — [4]) *Bull.* Roure Bertrand Fils, April 1921, 8. — [5]) *Bull. applied Bot.* 7 (1914), 697. As per *Bot. Zentralbl.* 128 (1915), 696. The abstract on basil oil published in *The Amer. Perfumer* 10 (1915), 265, without mentioning the source, pertains to this paper by Lubimenko and Novikoff which we dealt with in our *Report* 1916, 5. — [6]) Pfeffer, *Pflanzenphysiologie*, 2nd ed. vol. II, p. 117.

refraction (blue to ultraviolet) exercise the same influence on the plant development as does weakened mixed light, while red and yellow light causes the same alterations in the plant as continuous darkness. '

The emulsin obtained by aqueous maceration of almonds and precipitation of the extract with alcohol is a mixture of various enzymes containing, in addition to β-gluco-sidase (emulsin proper), lactase, gentiobiase, invertase, cellobiase, β-galactosidase, and other ferments. According to M. Bridel and R. Arnold[1]) it makes no difference in the preparation of emulsin whether ethyl alcohol, methyl alcohol, or acetone is employed. However, by varying the time during which the precipitant is allowed to act on the precipitate, emulsin preparations may be obtained in which some of the enzymes mentioned, e. g., lactase or invertase, are missing.

Physiological and pharmacological Notes.

In an elaborate paper entitled, *Die Riechstoffe und das Riechen* (On aromatics and the sense of smelling), A. Tschirch[2]) discusses the hitherto-known investigations and theories on the physiology and chemistry of the sence of smelling published by Zwaardemaker, H. Henning, Rupe and Majewski, Marchand, Ruzicka, and others. Basing on these investigations and his own experience, the author endeavours to answer the question: — Which are the conditions which must be complied with in order that a body shows an odour? Tschirch arrives at the following results: —

1. The phase of the aromatic must show a certain temperature, and it is likewise of importance whether the aromatic is dissolved, and which is the solvent.
2. The substance must be readily soluble in air.
3. The distribution-coefficient for the aromatic and air must be favourable for air, hence in case of a mixture of equal quantities of aromatics the odour of such bodies will predominate which are most soluble in air.
4. The distribution-coefficient for aromatic + air ←→ lipoid plasma of the olfactory cells must be favourable for the latter.
5. If it is assumed that chemical reactions are set up between the aromatic and the plasma, the former must contain atoms, atom groups, or ions which are able to react with the plasma molecules.
6. The osmophoric groups which generally are characterized by a strong tendency to react, are osmophoric only conditionally, at any rate only in cases when they are able to react with the colloidal plasm of the olfactory cells. The general chemical structure, more specially the building-up of the aromatic is of minor importance. A system of the shades of odour basing on the constitution of the various aromatics can not be established.
7. The sensation of odour is not caused by the aromatics, but by the very labile compounds formed in the colloidal olfactory cell-plasm (offering enormous surfaces) and mostly decomposing again instantaneously. These are either adsorption compounds — which is less probable —, or reaction-products between the aromatic (highly-ionised on account of its extreme dilution) and the olfactor cell-plasm which offers the aromatic a most extraordinary great surface in form of olfactory hairs, dimples, or conicles.

[1]) *Journ. de Pharm. et Chim.* VII. 23 (1921), 161. — [2]) *Schweizerische Apotheker-Ztg.* 59 (1921), Nos. 17 to 20. From a reprint kindly forwarded to us.

8. These are the compounds exercising the sensation of odour on the olfactory nerve which is then conducted to the brain.

9. Hence, quite a series of conditions must be complied with in case that an odour is to be rendered perceptible. If one of them is not answered to and there is a missing link in the chain, no odour is noticeable.

10. Odour is a chemical action on the sense of smelling.

Tschirch speaks of the "solubility of the substance in air". In order to explain this, scientifically incorrect, expression we add that the author refers to a paper published by H. Erdmann[1]) who inferred, from the easy solubility of aromatics in *liquid* air, a specific solubility of these bodies also in *gaseous* air. For the sensation of smell, not the volatility of the substance is deciding, but a different property which Tschirch terms solubility in air. The author wishes to point out hereby that the molecule of the aromatic, which emits a different odour when in concentrated and in diluted state, undergoes changes due to the air. With increasing dilution a cleavage down to the ions is expected to pass off, as in the case of aqueous solutions.

F. B. Hofmann[2]) has published a paper on the sense of smell basing principally on self-observation. Owing to a severe catarrh of the nasal cavity the author had nearly entirely lost his power of smelling, and but quite by degrees and very slowly normal smelling sensation was recovered. During this period (several years), Hofmann undertook systematically a large series of experiments, the result of which is as follows: —

In the beginning Hofmann was only able to perceive the odour of natural and of artifical musk in their characteristic peculiarity and apparently also in their full strength. Pyridine smelled strong, but not so unbearable as usually. Of other bodies, the author had a sensation of odour with acetone and, quite indefinite as to character, of *iso*butyl and *iso*amyl alcohols. When in the following weeks the sense for smelling pyridine improved noticeably (the author made use of Zwaardemaker's olfactometer as modified by Zimmermann), also other substances which hitherto were odourless for him became noticeable. Ammonia and trimethylamine smelled strong; diethyl ketone, acetone, amylene hydrate, ether, and chloroform somewhat less strong; butyl and amyl alcohols, amyl acetate, butyrate, and valerate very weak, and thymol, toluene, and xylene extremely weak. Only a trace of odour was noticed, *inter alia*, with benzaldehyde, carvacrol, menthol, and phenol; yet Hofmann was able to differentiate between the odour of these bodies. No odour whatsoever was perceptible with asa fœtida, iodoform, mercaptane, scatole, and vanillin.

Some months later Hofmann noticed that many of the substances mentioned showed a strong smell, but quite different from their usual character. Normal behaviour was exhibited, in addition to musk, only by vanillin. Indole remained quite odourless. The author was particularly struck by the qualitative change in the different smelling sensations after their reappearing. Violets and ionone, for instance, smelled in the beginning like cigar tobacco, later on the true violet odour became perceptible.

Even several years afterwards the author failed to perceive some special odour aracters. For him, putrefying albumen and scatole showed a faint sweetish odour, phuretted hydrogen, carbon disulphide, garlic, and various spices, such as caraway, abnormal, indefinite smell.

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[1]) *Journ. f. prakt. Chemie n. F.* **61** (1900), 226. — [2]) *Zur Theorie des Geruchsinnes, I. Parosmie-Studien. tschr. f. Biologie* **73** (1921), Nos. 1 to 4. As per a reprint kindly forwarded to us.

Hofmann concludes from his observations that most of the odoriferous substances act not only on a single, but on various peripheric receptive organs of different specific energy. Whenever a series of such receptive organs are acted upon and act together, combination smells are generated and the individual smells disappear more or less. The author considers this phenomenon to be the reason why some aromatics, when concentrated, show an odour different from that in diluted state[1]. By taking for granted that an odoriferous substances acts on several receptive organs it might be readily explained why the odours of many chemically pure substances resemble each other, and why from newly-synthesised bodies specific new odours result which otherwise are not to be found in Nature.

In a paper entitled, *Über einen historischen Beitrag zur Theorie der Geruchsempfindung* (On a historical contribution towards the theory of odour perception), H. Heller[2] cites and discusses a passage from a book published, in 1814, by C. W. G. Kastner, professor of physics and chemistry in Halle, and entitled, *Einleitung in die neuere Chemie* (Introduction into modern chemistry). The author proves that already more than one hundred years ago Kastner held views on perception of odour which highly resemble modern theories. Nowadays, we agree with Kastner that the senses of taste and of smell are in close relation to each other, and also that in both cases it is necessary for the actual sensation that the respective active body be virtually present. Likewise, Kastner's opinion is correct insofar that we are only able to smell gases. We are unable to perceive liquid aromatics by their smell in case they are introduced into the nose. In Kastner's opinion, sensation of odour is due to a disturbance of equilibrium. This, too, is correct. On the mucous membrane of the nose, the content of water in the membrane and in the surrounding air, under normal conditions, are in equilibrium; however, as soon as the inhaled air carries particles of an aromatic, the conditions of osmotic and the chemical equilibrium are upset which makes the basis of sensual perception[3]. Finally, Kastner maintains that the sensation caused on the nasal mucous membrane is more unequivocal and less subject to errors than the sensation of sight. Heller agrees with this view (hitherto not contradicted) and supports it by proofs, the discussion of which, however, would carry us beyond the scope of our *Report*.

The same author[4] demonstrates by various instances that chemical compounds which are generally said to show an offensive or unpleasant odour, when in a quite pure state, cause an entirely different and often even pleasant sensation of smell, sometimes, too, none at all. *Pure* acetylene, *pure* carbon disulphide, whose impurities show a putrid smell, show a pleasant ethereal odour. Likewise, various alkyl sulphides (*iso*amyl, ethyl sulphides), even ethyl mercaptane may be freed nearly entirely from their unpleasant smell by heating with copper powder (decomposition being but feeble); the latter adsorbs the evil smell. Hydrogen arsenide, whose garlic-like smell could be hitherto regarded as characteristic for that body, is according to Thoms and Hess[5] odourless when quite pure, and when applied to the tongue causes a feeble sweet taste. (Of course these experiments were carried out with infinitesimal quantities.) Heller points out that these facts have not received due consideration in some recent investigations, e. g., in those of Kauffmann and of Henning on odour sensations. Hence, Kauffmann's[6] theory of the change of odour (with alkylamines, mercaptanes,

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[1]) Cfr. the view held by Tschirch, preceding abstract. — [2]) *Deutsche Parfüm.-Ztg.* 7 (1921), 83. — [3]) Cf. for this the above-cited paper by Tschirch. — [4]) *Deutsche Parfüm.-Ztg.* 7 (1921), 123. — [5]) *Ber. d. deutsch. pharm. Ges.* 80 (1920), 488. — [6]) *Ztschr. f. Psychologie,* 2. Abt. 1908, 217.

thio-ethers, &c.) and likewise Henning's[1] theory of compound odours which is based on the formula and the odour of (impure) carbon disulphide, are both untenable.

The connection between constitution and odour are dealt with in a paper by M. Guerbet[2]).

In research work on olfactology it is of importance to examine at any given moment the condition of the observer's sense-organ. According to H. Zwaardemaker[3]) this is done best (1) by establishing the accessibility of the nose to the air in respiration; (2) by testing the sensitiveness of the sense-organ. Whether the nasal cavities are normal or not can be ascertained, as the author proved years ago[4]), by breathing quietly and briefly on a metal plate held below the nose. From the shape of the two breathing-spots each subdivided by a hiatus conclusions may be drawn as to the transmissibility of the air through the nose. The acuity of the smell-organ is measured by means of the olfactometer, which contrivance we described as early as in 1904[5]).

By means of an improved type of olfactometer the author found the following limit values for a normal olfactory organ, expressed in tube-lengths for a just appreciable smell-sensation of the aqueous solutions: — concentrated solution of amyl acetate, 0.17 cm.; conc. sol. of nitrobenzene, 0.19 cm.; 0.08 per cent. sol. of terpineol, 0.23 cm.; conc. sol. of artificial musk (trinitro*iso*butyltoluene), 0.18 cm.; 0.11 per cent. sol. of (commercial) allyl alcohol, 0.26 cm.; 0.26 per cent. sol. of guaiacol, 0.20 cm.; 0.32 per cent. sol. of caproic acid, 0.15 cm.; 0.38 per cent. sol. of pyridine, 0.11 cm.; conc. sol. of skatole, 0.28 cm. For obtaining a general notion of the sensitiveness of the observer's nose, the nickel supply-cylinder may be replaced by a piece of new indiarubber tubing 10 cm. long with an interior diameter of 8 mm. An olfactory organ may be considered to be normal when its "minimum perceptibile[5])" for new, unused, vulcanised caoutchouc lies at about 1 cm. of the olfactometrical scale.

A *camera inodorata*, in which olfactometric experiments may be carried out regardless of any by-odours, has been devised by H. Zwaardemaker[6]). The camera is a box with glass walls of a capacity of 400 litres, the roof and the bottom being of aluminium. All wooden parts are equally covered with this metal which absorbs odorous matter but slightly. The box is placed on high legs, and the experimenter can pass his head from below through an opening that can be closed by a slide. The space may be rendered inodorous in a short time by means of an uviol or preferably a quartz lamp. But few odours are not destroyed by ultraviolet light. As the author demonstrated, in 1913, in conjunction with Tempelaar[7]), many odorous bodies are extremely sensitive to light, *i. a.*, many esters, acetone, chloroform, borneol, eucalyptole, eugenol, citral, terpineol, vanillin, coumarin, butyl alcohol, pyridine, skatole. Some odour of ozone which may, be present after the illumination disappears soon.

An olfactometer is attached under the slide at the bottom of the box, by which olfactometrical determinations can be made. By means of special contrivances, the inner tube of the olfactometer can be readily freed from any adhering scent. The observer must have closely-cropped hair and a quite scentless skin. If necessary, the skin must be thickly powdered with talc, or covered with odourless vaseline. After

[1]) Henning, *Der Geruch.* Leipzig 1916. — [2]) *Journ. de Pharm. et Chim.* VII. 22 (1920), 344. As per *Chem. Zentralbl.* 1921, II. 414. — [3]) *Perfum. Record* 12 (1921), 308. — [4]) *Die Physiologie des Geruchs*, Leipzig 1895, p. 72. — [5]) Cf. *Report* October 1904, 104. — [6]) *Perfum. Record* 12 (1921), 243. — [7]) Cf. *Report* October 1913, 126.

this the observer remains in the box for five minutes (while the lamp radiates) with closed eyes screened by euphos-glass spectacles.

The experiments showed that in the *camera inodorata* the *minimum perceptibile* was on the average 25 per cent. lower than in ordinary surroundings.

The camera may be used also as a *camera odorata* by volatilizing a measured quantity of odorous substance and carrying out the olfactometric measurements in the scented atmosphere.

The firm of Lautier Fils, of Grasse, have constructed an appliance called "evapol-factometer" and designed for the recognition and valuation of odours. The apparatus was invented by Oddo[1]), and it consists of a thermometer, the mercury bulb of which is surrounded by an electrical resistance, and a very fine polished silver sheath. A rheostat above the thermometer permits of varying the current intensity, and hence the temperature. In use, the compound perfume liquid to be tested is poured on the silver rod and the temperature increased slowly. The separate odours are said to evaporate according to their degrees of volatility and may be perceived singly and one after another. This new process of analysing odorous bodies claims to offer various advantages over the usual method of testing by a spill of paper.

The sense of smell and the recognition of smells is rarely exercised and hence but feebly developed with most people. The following experiment was carried out at the Philadelphia College of Pharmacy and showed to which extent mistakes in recognizing smells occur even with skilled persons[2]). A series of 15 liquid odorous substances was submitted to twenty men, all with a more or less complete pharmaceutical training. The purpose of the test was to identify the odour of each specimen. Oil of turpentine was the substance which was best recognized, by all except three, which called it in turn, oil of anise, oil of caraway, and pine oil. Alcohol was difficultly recognized by the majority, on the other hand, vinegar[3]) was easily identified. Oil of cinnamon was reported by three persons as oil of anise, oil of bitter almond, and oil of wintergreen. Kerosene and gasoline were confusing to quite a number. Two men reported gasoline as chloroform, two others took kerosene for carbon disulphide. Creosote was judged by five as oil of clove, by five others as cresol. Only two men failed to identify methyl salicylate, who took it for oil of peppermint. Benzaldehyde was judged twice as nitrobenzene, oil of orange eight times as oil of lemon. One man took ether for ethyl nitrite. Linseed oil was recognized by nine persons, ten reporting it as fish oil or cod liver oil, and one taking it as neatsfoot oil. The identification of oil of nutmeg was not attempted by three of the men, three reported oil of turpentine, one reported it as oil of colander, and one as oil of cardamom. One of the students had no smelling sence for hydrogen sulphide and admitted that he detected only the most powerful odours.

On former occasions, we reported on the interesting investigations by K. von Frisch[4]) on the *sense of smell in bees*. The same author[5]) publishes now numerous new experiments on the "sign-language" of the bees. It could not be established beyond doubt whether the bees communicate by means of sounds; at any rate, however, the author was able to prove that the bees inform each other on the presence of food by some sort of sign-language. This communication is effected, in accord with the darkness in

[1]) *Perfum. Record* 12 (1921), 135. — [2]) R. R. Foran, *Amer. Journ. Pharm.* 93 (1921), 683. — [3]) According to Weiss, vinegar acts not on the olfactory organ, but on the sense of touch. Cf. *Report* October 1915, 70 — [4]) *Reports* 1917, 121; 1919, 108. — [5]) *Münch. med. Wochenschr.* 1920, p. 566; 1921, p. 509. As per a separate copy kindly forwarded to us.

the bee-hive, not by the sence of sight, but by touch. As soon as a bee (the collector) has discovered a food-place, it performs a "searching dance" when returned to the hive, which causes the others bees to swarm out in all directions and to search for the food-place. In cases where the crop emanates a blossomy smell the latter is noticed with the searching bee, and this smell is then traced. When the crop is abundant the collecting bee assists the others in searching by exhibiting its own smell-emanating organ (located between the 5. and 6. back segment of the body), and thus impregnating the surrounding of the food-place with its own smell.

About 40 essential oils have been investigated by Heinz[1]), of the Pharmacological Laboratory at Erlangen, with regard to their *pharmacological action*. Although the oils are frequently mixture of quite different components, they often show the same action, insofar as the latter is based upon identical physical properties of the oils, *e. g.*, volatility and solubility of lipoids. For instance, the odoriferous bodies have in common both the properties of local irritation, lasting, however, only a short time, and that of chemotaxis, *i.e.*, the attractive action on leucocytes. Owing to the solubility of the essential oils in lipoids, fats and oils, they easily permeate the skin protected by a layer of fat and hence assailable only with difficulty. Equally, the aromatics spread rapidly in the blood, since they combine readily with the blood corpuscles rich in cholesterol and circulate with them.

Of details, Heinz deals with the action of peppermint oil on the liver[2]), of juniper oil on the kidneys, of thymol on the dental nerves, and of turpentine oil on the leucocytes. We content ourselves with this reference, as we have frequently reported on the pharmacological properties of these and of other essential oils[3]). Yet we wish to add that Heinz recommends an emulsion of milk with 5 per cent. turpentine oil for hypodermic injection, and that he introduces a powder for dressing wounds composed of sugar with 5 per cent. turpentine oil, which he terms "terpestrol".

J. C. C. Gunn and O. H. Plaut[4]) furnish some details on the *carminative action* of various essential oils, which, however, seem to contradict each other. According to Gunn, essential oils such as anise, peppermint, fennel oils, &c., when diluted 1 : 20 000, stop the peristaltic motion entirely. The same action is effected by local application of 0.5 cc. of a solution of 0.05 per cent. of the oils in Ringer's solution. The therapeutic action consists in: relaxation of the cardia, alleviation of excessive peristaltic movements, besides local irritation, such as hyperæmia and sensation of heat.

On the other hand, Plaut noticed, with an isolated bend of a dog's bowel *(in situ)*, marked increase of the peristaltic motion. Previous treatment with atropine effected lessing of the motion, application to the bowel of cocaine neutralized the action completely, and morphine was without any influence on the action of the essential oils. No explanation is given for this discrepancy which may be caused by the method adopted, or by the different action of different doses.

A short paper by F. Marre[5]) deals with the use of aromatics as *sedative remedies*. Aromatics of animal origin, such as musk, civet, castoreum, and ambra are known ever ᵌce on account of their sedative action. Fumes of ambra were employed as a remedy epilepsy, and later on inhalations of ambra were proved to possess an anti-asmodic effect.

[1]) *Münch. med. Wochenschr.* 68 (1921), 628. As per *Deutsche Parf. Ztg.* 7 (1921), 157. — [2]) Cf. *Bericht* ᵗᵐ. ed.) 1921, 38. — [3]) Cf. our *Reports* under the heading *Pharmacological and physiological Notes.* — *Iourn. pharm. and exper. Therap.* 16 (1920), 39 and 311. As per *Therap. Halbmonatsh.* 35 (1921), 184. — *Parfum. moderne* 14 (1921), 80.

Of odours of vegetable origin showing a sedative action, the author enumerates the lily, lily of the valley, carnation, orange, opopanax, vanilla, and heliotrope. Various blossoms, such as the lily, tuberose, and honeysuckle, are known to exercise a stupefying action; by experimenting on animals the essential oils were proved to possess, with the living organism, a similar action as chloroform or ether[1]).

Sores of various kinds have been treated in sixty-eight cases successfully with terpeneless oil of lavender[2]). If the greater part of the infected sores show no inflammatory symptoms after several applications of the pure oil, it is then desirable to resort to weaker solutions (1 to 10 per cent.). Gangrene was arrested immediately, and in many instances cicatrisation was complete in less than a month. In the case of varicose ulcers in particular, a weak solution has proved an excellent antiseptic. Very good results were obtained particularly with burns and scalds by the application of the terpeneless oil for four or five days, followed by wet dressings during four or six days, and finally dressing with starch powder or bismuth. In the case of chancrous sores, the pure oil was applied, and then a powder of thymol iodide and dry dressing. In other cases, after removing the pus, the pure oil was injected and the sore covered with a pad damped with the oil; this was renewed daily, and finally a dry dressing applied after cleansing the sore.

G. and K. Cori[3]) report on the treatment of febrile tuberculosis of the lungs with intramuscular injections of *menthol + eucalyptus oil*. The authors injected two to three times a week 0.5 to 1.0 cc. of the following mixture: — 0.1 g. iodine, 0.5 g. camphor, 10.0 g. menthol, 10.0 g. eucalyptus oil, 20.0 g. castor oil, and give the result of the treatment of 168 poor or indigent patients as follows: — *(a)* Patients with tuberculosis of the second and third stage, as well as infantine tuberculosis, can in many cases be freed from fever by means of Berliner's mixture[4]), so that they mostly may undergo a treatment with "alt-tuberculin" without contracting fever. *(b)* The suppression of fever passes off lytically and without unpleasant consequences of any kind. *(c)* If during a tuberculin-treatment continual fever occurs, injections according to Berliner enable further application of tuberculin by depressing the fever. *(d)* Regardless of the lowering of the fever, the subjective complaints, such as pain, cough, or night perspiration, &c., were in all cases alleviated or even removed. *(e)* A rise in temperature after injections of tuberculin have no bad influence upon the action of tuberculin in the second stage of pulmonary tuberculosis, whereas in the third stage a rise in temperature is generally associated with loss in weight, hemoptœa, &c. *(f)* The fever-depressing action of the Berliner mixture passes off by action on the pulmonary seat of the disease as being the cause of the fever. This was proved by experiments which demonstrated that during the treatment with the Berliner mixture the cutaneous sensitiveness towards tuberculine showed a decrease.

As has been shown by Macht[5]) the *antispasmodic action* of the combined opium alkaloids is due to the presence of the benzyl nucleus in the alkaloids of the papaverine group. Simpler compounds containing the benzyl nucleus, such as benzyl alcohol, some of its esters, and benzaldehyde, but not benzoic acid, have the same action. The antispasmodic properties are exhibited, as is demonstrated by H. A. Shoule

[1]) Detailed studies on the after-effects on, and poisoning of, the olfactory sense have been published also by Henning. Cf. *Report* 1916, 103. — [2]) Marchand, *Perfum. Record* 12 (1921), 153. — [3]) *Therap. Halbmonatsh.* 35 (1921), 236. — [4]) Cori's recipe differs somewhat from the prescription given originally by Berliner. — [5]) *Journ. of Pharmacol. and exp. Therap.* 9 (1917), 287; 11 (1918), 263.

and P. Q. Row[1]), in a higher degree by veratryl and piperonyl alcohols, piperonal, vanillin, veratryl aldehyde, and *q*- and *p*-hydroxybenzaldehyde.

Since nothing is known as to the therapeutic action of the benzyl esters of the higher fatty acids and the aliphatic and aromatic amino-acids, and other sulpho and amino-acids, the authors prepared a number of these esters, and determined the physical and therapeutical properties. The esters of the higher fatty acids were tasteless, colourless liquids — those of the unsaturated acids showed an unpleasant taste — or low-melting solids, which had neither an anesthetic effect nor an irritating action on the mucous membrane. Owing to the insolubility in water of these esters the usual physiological tests on animals were not entirely satisfactory. Clinical tests were therefore resorted to, which demonstrated the antispasmodic action of these esters in asthma, dysmenorrhœa, high blood pressure, pylorospasm, and spastic constipation.

The benzyl esters of *p*- and *m*-amidobenzoic acid showed an irritating effect on the mucous membrane and possessed local anesthetic properties.

Benzyl lactate was also prepared but because of its irritating effect it was not tested clinically.

The benzyl esters of mixtures of fatty acids derived from natural fats had the equal therapeutic properties as the benzyl esters of the individual fatty acids. They are more readily hydrolysed by lipase than are the benzyl esters of aromatic acids.

As C. Nielsen and J. A. Higgins[2]) have observed, the *peristaltic movements* (observed *in situ* with dogs) are lessened by intravenous infection of a 5 per cent. emulsion of benzyl benzoate or cinnamate. The latter ester is at least quite as effective as the benzoate, but is not quite so effective in lowering the blood-pressure. Benzyl cinnamate shows a moderately toxic action; a small dog stood about 15 gms. after oral application without any harm.

Fröhlich and Grossmann[3]) continued their experiments on the medicinal *action of camphor*[4]). A frog's heart, when under camphor treatment, reacted no more, on application of alternating current, by raging *("wühlen")*. The authors conclude herefrom that camphor is capable of improving the metabolism of the heart ventricle.

G. Joachimoglu[5]) was able, by application of camphor to a leech preparation, to effect increase of the tonus, and contractions of hours' duration. *D-*, *l-*, and *d,l*-camphor showed the same action. Since thymol, of anthelminthic fame, causes a similar effect, the author believes camphor to be efficacious as vermifuge when applied as enema.

Terpichin (a solution of 15 per cent. turpentine oil with each 0.5 per cent. of quinine and anesthesine in olive oil) is used for *dermatological purposes* and with various inflammations. W. Karo[6]) prefers the intravenous injection of this remedy in lieu of the usual intragluteal application, since it proved to be superior to the latter.

Trabut[7]) recommends in the *treatment of diabetes* a decoction of eucalyptus leaves (10 to 15 gr. to a litre of water and boiled down to one-half of its volume). The leaves of *Eucalyptus diversicolor* and *E. rostrata* act as well as those of *E. Globulus*.

As to the medicinal use of *turpentine oil*, see p. 77 of this *Report*.

On injections with solutions of *benzyl benzoate*, vide p. 92 of this *Report*.

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
[1]) *Journ. Amer. chem. Soc.* **43** (1921), 361. — [2]) *Journ. of laborat. and clin. med.* **6** (1921), 388. As per m. *Zentralbl.* **1921**, III. 1173. — [3]) Cf. *Bericht* (Germ. ed.) **1921**, 63. — [4]) *Arch. f. exp. Pharm. u. Path.* (1921), 1. As per *Therap. Halbmonatsh.* **35** (1921), 376. — [5]) *Arch. f. exp. Pharm. u. Path.* **88** (1920), 364. As : *Therap. Halbmonatsh.* **35** (1921), 376. — [6]) *Klin. Wochenschr.* **1** (1922), 89. — [7]) *Perfum. Record* **12** (1921), 265.

Chemical Notes.

In a paper entitled, "Some constituents of essential oils and their structural relations", J. W. D. Hackh[1]) endeavours to give an outline of the structural relation of the above-mentioned constituents, and to illustrate by practical application the advantages of structure symbols, the new chemical notation of organic compounds, the present method of notation occupying a vastly greater space and annoying the printer in a high degree. The old formulæ are replaced by geometrical devices which eliminate the customary symbols C, H, O, N and represent their atoms by points from which one, two, three, or four lines, respectively radiate. A straight line — stards for hydrogen (H—H, assuming one atom of hydrogen at either and of the stretch), an angle $>$ represents water $\left(\substack{H\\H}\!\!>\!O\right)$, the sign —$<$ stands for ammonia $\left(H—N\!<\!\substack{H\\H}\right)$, and a cross $+$, for methane $\left(\substack{H\\|\\H—C—H\\|\\H}\right)$. Where two stretches meet, one atom of oxygen is located, where three or four meet, an atom of nitrogen, or carbon, respectively. Each organic compound belongs to a different type and a different class, such as hydrocarbons (o—, or R—H, the circle standing for the radical), alcohols (o—↗, or R—OH), aldehydes (o–↗, or R—CHO), &c. The type of the compound indicates its chemical character and reactivity, the class its general structural characteristics, either saturated or unsaturated, aliphatic or aromatic. Expressed by the new notation, $+\!+$ stands for ethane CH_3—CH_3, for ethylene $CH_2=CH_2$, for hexamethylene C_6H_{12}, for benzene C_6H_6, for menthane, and for camphor, &c.

These examples seem sufficient to give the reader an idea of Hackh's notation. Those who are interested in the study of the new system may resort to the original paper, where the notation of 157 compounds occurring in essential oils is given and their structural relation is detailed.

The salts of the higher fatty acids, when in solution, crystallise in the shape of a spongy mass which, according to C. A. Cofman-Nicoresti[2]), shows a great power for absorbing volatile oils. As little as 5 per cent. of the salts was sufficient for obtaining such "solid solutions".

Hydrocarbons.

A process for obtaining *aromatic hydrocarbons* has been devised by A. S. Ramage[3]):— Hydrocarbons containing one or more alkyl groups are treated, in the presence of a catalyst, such as ferrous oxide, with hydrogen. The alkyl groups are hereby replaced by hydrogen.

A process for the preparation of *polycyclic hydrocarbons of the terpene series*, for which a patent is applied by the firm of Schering, of Berlin[4]) consists in heating the

[1]) *Journ. Amer. pharm. Ass.* 9 (1920), 948. As per a separate copy kindly forwarded to us. — [2]) *Chemist and Druggist* 95 (1921), 854. — [3]) Am. Pat. 1 365 849 of Jan. 18th, 1921. As per *Chem. Zentralbl.* 1921, II. 558. — [4]) Germ. Pat. Appl. C/29 518, published Jan. 12th, 1922.

hydrazones of terpene ketones with mercuric oxide, or the double salts of mercuric chloride and the hydrazones, after addition of the equivalent amount of alkali, in an indifferent solvent. By the interaction of the mercuric oxide and the hydrazones, difficultly-soluble basic mercury compounds are formed whose constitution possibly resembles that of the mercuri-ammonium compounds and which decompose, on heating in indifferent liquids, according to the following equation:—

$$C_{10}H_{16} : N \cdot NH \cdot Hg \cdot OH \longrightarrow C_{10}H_{16} + N_2 + Hg + H_2O.$$

The patent specification contains details for the preparation of tricyclene from camphor hydrazone (crude yield, 78.3 per cent.), of d-*cyclo*fenchene from *d*-fenchone hydrazone, and of *apo*cyclene from camphenilone hydrazone.

The principal products resulting from the pyrogenetic decomposition of *benzene* are, according to E. Peytral[1], hydrogen and diphenyl; $2C_6H_6 \longrightarrow C_6H_5 \cdot C_6H_5 + H_2$. One-third of the hydrogen formed results either from a radical decomposition of part of the benzene into methane, carbon (graphite), and hydrogen, or (as is more probable) from a part of the diphenyl formed and then decomposed further.

Benzaldehyde, when submitted to the treatment indicated, decomposed principally into benzene and carbon monoxide, besides into diphenyl, carbon monoxide, and hydrogen. In addition, a small amount of anthracene is formed due to condensation in the hydrogen atmosphere. As secondary products of the decomposition of diphenyl, carbon and methane were traced.

A process for obtaining p-*cymene* from the waste terpenes (b. p. about 175°) resulting from the camphor synthesis, or the fractions boiling at 175° and at 160° of Swedish or Polish "turpentine" (pine) oils has been published by the Rheinische Campherfabrik[2], of Düsseldorf. The respective fractions are chlorinated slowly at temperatures ranging from 10 to 80°, the reaction-product distilled with steam, the volatile oil heated with some zinc chloride and subjected to distillation. Yield about 60 per cent. of the primary material; it may be raised to 75 per cent. by heating the crude material with an inorganic or organic acid, or an acid salt, and by using the fraction boiling at 175° for the chlorination.

Ralph H. McKee and Leland J. Lewis[3] recommend *fat-splitting reagents obtained from cymene, i. e.,* cymene stearosulphonic acid. The compound is obtained analogous to Twitchell's[4] method for preparing aromatic stearosulphonic acids. 280 gr. of oleic acid and 140 gr. of cymene were stirred, and 300 gr. of sulphuric acid (66 deg. Bé.) was gradually added, keeping the temperature below 35°. Further details on the preparation and purification of the product may be gathered from the original paper.

On comparison with Twitchell's reagent, benzene and naphthalene stearosulphonic acids, and the "Kontakt" reagent, the cymene derivative offers, in the opinion of the authors, the following advantages:— It is more easily and cheaply made and can be produced as a uniform product. The fatty acids as well as the glycerin obtained by its use are both of a lighter colour.

Terpinene. — Contrary to the other nitrosites of unsaturated bodies, whose structure is mostly bimolecular, the nitrosite of terpinene possesses the simple molecularity of $C_{10}H_{16}O_3N_2$, and it does not show the colour reactions characteristic of the dissociation

[1] *Bull. soc. chim.* IV, 29 (1921), 44. — [2] Germ. Pat. 819162 and 319163, July 14th, 1921. Engl. Pat. 156329, Febr. 3rd, 1921. — [3] *Americ. Perfumer* 16 (1921), 175. — [4] *Journ. Americ. chem. Soc.* 22 (1900), 22.

of the bisnitroso group. Since, however, the nitrosite, on treatment with caustic potash, gives rise to a body $C_{20}H_{31}N_3O_4$ (m. p. 163 to 164°), and since it interacts with amines, with formation of nitrolamines —C(:NOH)—C(·NHR)= and splitting-off of NO_2H, Wallach[1]) at a time was of opinion that terpinene nitrosite is bimolecular, at least in the solid state, and that the grouping NO_2 was attached to the carbon atom by the usual nitrite-linking C—ONO, as in the genuine nitrosites. This view is not shared by H. Wieland and F. Reindel[2]). The behaviour of di*cyclo*pentadiene and

$$\overset{\displaystyle -C\!-\!\!-\!\!-\!\!-C-}{\underset{(N_2O_3)}{\underset{\displaystyle -C\!-\!\!-\!\!-\!\!-C-}{\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{}}}}}$$
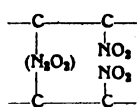
of ethylene shows that on addition of nitrogen trioxide N_2O_3 to unsaturated bodies *pseudo*nitrosites (*bis*nitroso-nitro compounds) are formed, of the structure as given by the annexed formula. Equally terpinene = $\varDelta^{1,3}$-dihydrocymene containing a grouping of two conjugated double-bonds, is no exception to this rule. By catalytic hydrogenation of terpinene nitrosite (m. p. 153 to 154°), Wieland and Reindel obtained, besides a monovalent base, a diamine which was found to be 1,2-diaminohexahydrocymene and which was identified by its dibenzoyl compound (I, m. p. 165°) and the hydrochloride of the monobenzoylated diamine (m. p. about 290°, turning brown). Hence, terpinene nitrosite undergoes a partial reduction to 1,2-diaminohexahydrocymene, and both the NO- as well as the NO_2-group are linked to the carbon atom by their nitrogen. By this reaction the structured formula (II) is established beyond doubt, where the authors have replaced the :C:NOH-group by the group $\overset{:C\!-\!\!-\!NH}{\underset{O}{\diagdown\diagup}}$ in order to indicate the insolubility in alkali.

The interaction with alcoholic potash studied by Wallach[3]) and yielding the nitrite must be considered to be an intramolecular alkylation, and formula (III) must be attributed to the reaction product. The body $C_{10}H_{15}O_6N_3$ obtained by Amenomija[4]) by action of nitric acid on terpinene nitrosite is, in the opinion of the authors, 1,2,2-trinitrotetrahydrocymene.
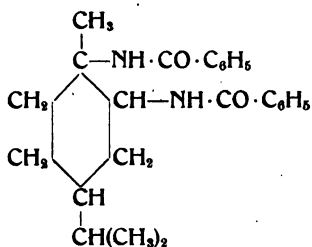
(I) Dibenzoyl-1,2-diaminohexahydrocymene.   (II) Terpinene nitrosite.   (III) Reaction product from terpinene nitrosite.
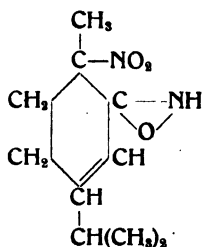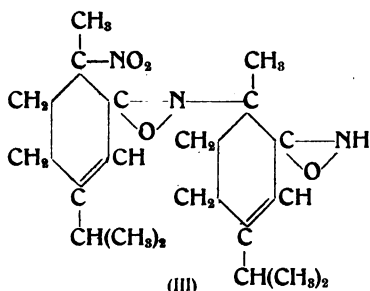
On *moslene*, see p. 51 of this *Report*.

Verbenene. — In a prior publication, Blumann and Zeitschel[5]) had proved that verbenol (I) splits off water readily on treatment with acid reagents and yields a doubly-unsaturated bicyclic terpene $C_{10}H_{14}$, verbenene. The authors prove now[6]) that verbenene, which is isomeric with *p*-cymene and which can be transformed into that terpene, possesses the structure of a dehydro-α-pinene (II). By oxidation by means of alkaline permanganate solution, verbenene was degraded to *cis*-norpinic acid (III) by which the intactness of the tetracyclic system was proved. The conjugated position of the

[1]) *Liebig's Annalen* 356 (1907), 223. See also *Report* April 1907, 142. — [2]) *Liebig's Annalen* 424 (1921), 92. — [3]) *loc. cit.* — [4]) *Berl. Berichte* 38 (1905), 2020. — [5]) Cf. *Report* October 1918, 105. — [6]) *Berliner Berichte* 54 (1921), 887.

double bonds was proved by the formation of the terpene from verbenol (I), by the value found for the molecular refraction (44.57, calc. for $\sqrt{2}$ 43.05), and by the behaviour of verbenene towards bromine. The easily-obtainable dibromide was strongly optically active, the rotation being opposite to that of the primary material, and gave rise, on treatment with dilute potash solution, to an unsaturated glycol $C_{10}H_{16}O_2$ (IV; m. p. 141°) and to an apparently oxide-like body which was not examined further. The authors were unsuccessful in trying to replace the bromine atoms by hydrogen. On the other hand, dihydroverbenene (V; b. p. 158 to 159° [726 mm.]) was formed on treating the terpene with sodium and alcohol. (Cf. Semmler, On the reduction of α-phellandrene, *Berl. Berichte* **36** [1903], 1035 and 1753.) Dihydroverbenene, which may be taken for a δ-pinene, strongly resembled α-pinene in its physical and chemical properties, such as the formation of pinene hydrochloride on introducing dry hydrogen chloride, or of a nitroso body identical with nitrosopinene from the nitrosochloride. Hence the authors believe that α-pinene is primarily formed by the action of acid reagents.

(I) Verbenol.   (II) Verbenene.   (III) Norpinic acid.

(IV) Glycol from verbenene dibromide.   (V) Dihydroverbenene, δ-pinene.   (VI) α-Pinene.
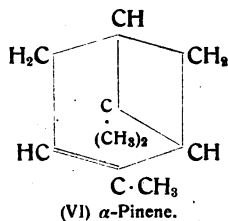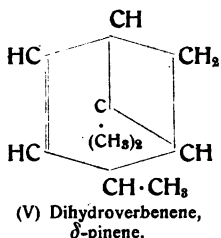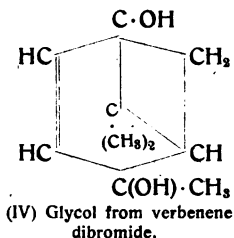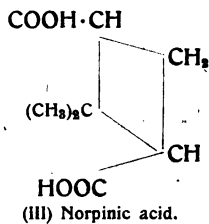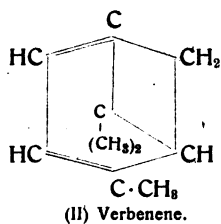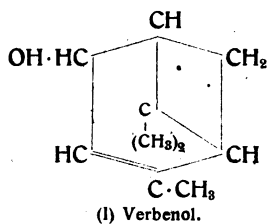
Pinene. — By repeated fractional distillation, *in vacuo*, of 15 litres of French turpentine oil, Pariselle[1] obtained: — α-pinene, b. p. 153.5 to 154.5° (760 mm.), or 62° (32 mm.), d_{00} 0.8748, $[\alpha]_{D15°}$ — 43,48°, $n_{D18°}$ 1.4690, rot. disp. 1 ($\lambda = 589$), 1.185 ($\lambda = 546$), 1.44 ($\lambda = 492$), 2 ($\lambda = 436$), coefficient of viscosity 0.0141, mol. refr. 43.85, and β-pinene, b. p. 163 to 164° (760 mm.), or 71.5° (34 mm.), d_{00} 0.8848, $d_{15°}$ 0.8728, $[\alpha]_{D15°}$ — 19.80°, rot. disp. 1 ($\lambda = 589$), 1.1 ($\lambda = 546$), 1.15 ($\lambda = 492$), 1.08 (?) ($\lambda = 436$).

With hydrogen bromide, α-pinene yielded the solid pinene hydrobromide, m. p. 94°, b. p. 94° (12 mm.), $[\alpha]_{D15°}$ + 27.95° (in toluene solution), and a liquid hydrobromide which contained the solid isomeride in the dissolved state. β-Pinene showed exactly the same behaviour and gave a solid monohydrobromide with nearly the identical physical constants, except $[\alpha]_{D15°}$ being — 31.50°. By the action of bromine on α-pinene Pariselle obtained the solid monohydrobromide, a liquid monohydrobromide, a dibromide m. p. 150°, with slight decomposition at 130°), and Wallach's dibromide (m. p. 166 to 168°)[2].

By synthesising pinocamphone and α-pinene from monocyclic bodies, L. Ruzicka and H. Trebler[3] were able to prove the correctness of Wagner's pinene formula (I),

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[1] *Compt. rend.* **172** (1921), 1496. — [2] Cf. *Liebig's Annalen* **264** (1891), 7. — [3] *Helv. chim. acta* **4** (1921), 666.

which hitherto was not quite fully established. By condensing the ethyl ester of pinonic acid with chloroacetic ester according to the method devised by Darzens[1]) the authors obtained the corresponding glycidic dicarboxylic ester and thence by saponification the acid itself (II; m. p. 128° with evolution of carbon dioxide). When this acid was heated to 230° it splitted off carbon dioxide and passed over into homopinocamphoraldehydic acid (III; b. p. 130 to 140° [3 mm.]; semicarbazone, m. p. 193 to 194°) which on oxidation with permanganate yielded homopinocamphoric acid (IV; diethyl ester, b. p. 130° [1 mm.]). This acid was best transformed into pinocamphone (V) by the method of W. Dieckmann[2]),
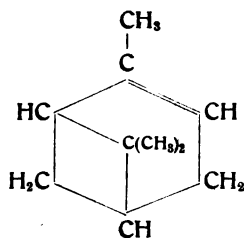
(I) Pinene.
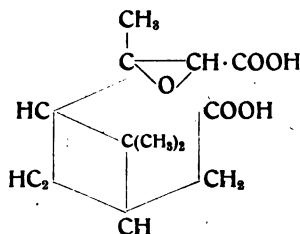
(II) Glycidic dicarboxylic acid from pinonic acid.
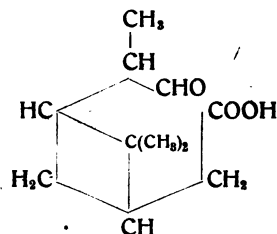
(III) Homopinocamphor-aldehydic acid.
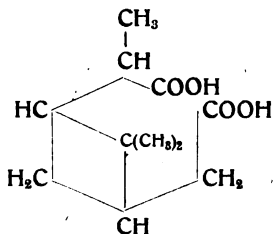
(IV) Homopinocamphoric acid.
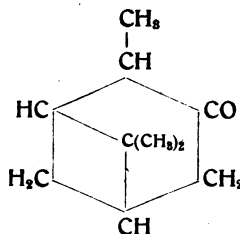
(V) Pinocamphone.

by condensation of the diethyl ester of the (IV), in xylene solution, with sodium. The ketonic acid ester formed primarily was saponified, with formation of pinocamphone, by boiling with a 15 per cent. hydrochloric acid. The semicarbazone and the oxime of the d,l-pinocamphone thus obtained were identical (as was proved by the melting-point of the pure substance and of the mixture) with the corresponding preparations of Wallach[3]) resulting from a d,l-pinocamphone from nitrosopinene by treatment with zinc and acetic acid. Since pinocamphone may be transformed into pinylamine and α-pinene by means of the reactions described already by the authors[4]), an uninterrupted way is given for the partial synthesis of α-pinene from α-pinonic acid.

Hitherto it has been generally taken for granted that on addition of dry hydrogen chloride to pinene always pinene hydrochloride = bornyl chloride (I) is formed. O. Aschan[5]) proved this assumption to be incorrect, as the isomeric liquid, *tertiary* pinene hydrochloride is formed in this reaction. This compound, stable only at a temperature below —10°, partly splits off hydrogen chloride on treatment with aniline and yields pinene rotating in the same sense as the starting material. When the tertiary pinene hydrochloride is removed from the freezing mixture, it rises in temperature up

[1]) *Compt. rend.* 139 (1904), 1214. — [2]) *Liebig's Annalen* 317 (1901), 27. — [3]) *Ibidem* 304 (1898), 287. — [4]) Cf. *Bericht* (Germ. ed.) 1921, 106. — [5]) *Vetenskaps Akad. Förhand.* 67, part A. 1914, No. 1. As per *Chem. Zentralbl.* 1921, III. 629.

to 60 to 80° and rearranges itself to solid bornyl chloride. It is probable that whenever bornyl chloride is formed from pinene and hydrogen chloride, the unstable compound (III) is always formed intermediarily.

Nopinene, when submitted to the same treatment, equally gave rise to the identical tertiary pinene hydrochloride which with aniline passed over into pinene and not into

(I) Bornyl chloride.

(II) Tertiary pinene hydrochloride.

nopinene. Since with the tertiary chloride the velocity of its rearrangement, at 0°, exceeds its formation velocity from pinene and hydrogen chloride, it was not possible, even at a low temperature, to obtain it free from bornyl chloride. Its odour is strangely suffocating, and it attacks the mucous membranes. The mixture of hydrocarbons obtained on scission with aniline consists mainly of pinene, but contains also some dipentene, or limonene, and a still unknown cyclic terpene (in the fraction b. p. 162 to 167°).

The action of hypochlorous acid on pinene, examined years ago by Wagner[1]) and his collaborators, has been investigated afresh by G. G. Henderson and J. K. Marsh[2]). These authors found that the products obtained formerly, two chlorohydrins, pinol oxide, sobrerythritol, and nopinol glycol, are not the primery products of the reaction, but are formed from these by the action of the potassium hydroxide employed. Treatment of pinene (b. p. 156 to 157°) with a very dilute aqueous solution of hypochlorous acid yielded two crude products of which the one was soluble in water. This product was a mixture of three crystalline dichlorohydrins, $C_{10}H_{18}O_2Cl_2$, which melted at 139 to 140°, 124 to 126°, and 155° respectively, together with a viscous, oily substance. The first of these dichlorohydrins (nitrobenzoate, m. p. 175°) gave reactions identical with those of the compound (m. p. 136°) prepared by Wagner and Slawinski. By direct synthesis of sobrerol dichloride (cis-1,2-dichloromenthane-6,8-diol, m. p. 138°) from i-sobrerol the authors confirmed Wagner's view that pinene dichlorohydrin (m. p. 139°) and sobrerol dichloride (m. p. 136°) are identical. (The mixture of both bodies showed the same m. p. 138°).

On treatment with two molecules of aqueous caustic potash, the dichlorohydrin (I), m. p. 139°, formed pinol oxide and i-pinol glycol-2-chlorohydrin (III) $C_{10}H_{17}O_2Cl$ (m. p. 104 to 105°) which after heating with caustic potash solution gave rise to pinol oxide. An

(I) Pinene dichlorohydrin (m. p. 139°).

(II) Isomeric intermediary (?) product, chlorohydrin (m. p. 70 to 71°).

(III) Pinolglycol-2-chlorohydrin (m. p. 104°).
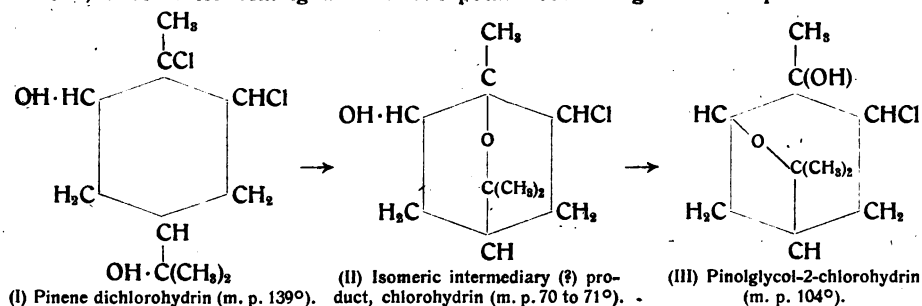
isomeric, but entirely different chlorohydrin $C_{10}H_{17}O_2Cl$ (m. p. 70 to 71°; nitrobenzoate, m. p. 125°) was formed on shaking one mol. of the dichlorohydrin (m. p. 139°) with one mol. potassium oxide in a very weak aqueous solution. This body was readily transformed, by the action of water, into i-pinolglycol-2-chlorohydrin, m. p. 104°. It may

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[1]) Cf. Reports October 1896, 88; October 1899, 63. — [2]) Journ. chem. Soc. 119 (1921), 1492.

be assumed that the compound of the m. p. 70 to 71° results as an intermediary product in the preparation of pinolglycol-2-chlorohydrin from pinene dichlorohydrin (m. p. 139°).
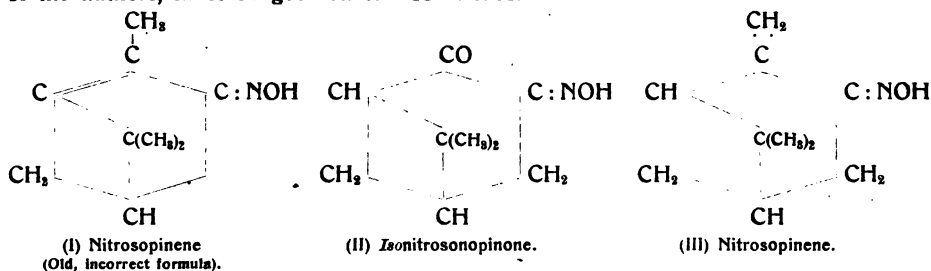
The dichlorohydrin of the m. p. 124 to 126° was optically active ($[\alpha]_{Hg}$ — 28,2°) and was apparently 2,8-dichloromenthane-1,6-diol. With dilute aqueous potassium hydroxide it yielded optically active pinolglycol-2-chlorohydrin (m. p. 131°), some *i*-pinolglycol-2-chlorohydrin (m. p. 104°), and a trace of pinol oxide. The third dichlorohydrin, m. p. 155°, was present only in a very small quantity and was likewise optically active ($[\alpha]_{Hg}$ — 59.5°); it is perhaps a derivative of *β*-pinene, a little of which may possibly have been present in the pinene used.

The viscous, oily body (see above), when treated with a 10 per cent. potassium hydroxide solution, yielded pinolglycol (m. p. 124°), which was evidently formed from pinol oxide and furthermore from a dichlorohydrin.

Fractional distillation *in vacuo* of the oily primary product which remained undissolved in water yielded, besides some unchanged pinene, some tricyclene dichloride, $C_{10}H_{16}Cl_2$, m. p. 169 to 172°, identified by conversion into camphane, m. p. 154 to 155°.

In a third paper on pinene[1]), L. Ruzicka and R. Trebler[2]) were able to disprove the formula (I) for *nitrosopinene*, as suggested by Wallach[3]). It had been Wallach's intention to explain, by aid of his formula for nitrosopinene, various cases of isomerism which occur in connection with various derivatives of nitrosopinene. The nitrosopinene obtained from the nitrosochloride is different from the nitrosopinene prepared from the former *via* pinylamine, pinocarveol, pinocarvone. Likewise, the amine formed on reduction of the oxime is not identical with pinylamine. In order to explain these differences in the oximes and amines, Wallach had suggested that when nitrous acid acts on pinylamine a migration of the endocyclic double linking into the semicyclic position takes place. Ruzicka and Trebler proved now that on ozonisation nitrosopinene yields an ozonide which on splitting up is transformed into formaldehyde (or formic acid) and *iso*nitrosonopinone (II, semicarbazone, m. p. 220°). From the ozonide of acetylpinylamine there results, by the same treatment, the acetyl derivative of *α*-aminonopinone, m. p. 120 to 121°. It follows from these reactions that in nitrosopinene (III) and pinylamine the double bond is in semicyclic position and that both bodies are derivatives of *β*-pinene. This new formula for nitrosopinene is in accord with Bredt's rule according to which camphor derivatives, on stereochemical grounds, are non-capable of existance, whenever a double bond proceeds from a carbon atom which is in common with two rings.

Since pinene nitrosochloride is optically inactive, the two oximes, in the opinion of the authors, must be geometrical isomerides.


(I) Nitrosopinene (II) *Iso*nitrosonopinone. (III) Nitrosopinene.
(Old, incorrect formula).

¹) Cf. *Bericht* (Germ. ed.) 1921, 106. — ²) *Helvet. chim. acta,* 4 (1921), 566. — ³) *Liebig's Annalen* 389 (1912), 185

Camphene. — The body m. p. 157° known generally in literature as camphene hydrochloride resulting from the treatment of camphene with an excess of gaseous hydrogen chloride should be termed appropriately *isobornyl chloride*, as we learn from a patent application by the firm of Schering[1]), since it is a stereoisomeride of pinene hydrochloride, or bornyl chloride. The true *camphene hydrochloride* (hitherto unknown), *i. e.*, the primary addition product of hydrogen chloride to camphene, is easily obtained by the action of hydrogen chloride on a solution of camphene, when care is taken to avoid any excess of the acid.

$$H_2C - CH - C(CH_3)_2$$
$$| \quad CH_2 \quad |$$
$$| \quad | \quad CH_3$$
$$H_2C - CH - C{<}^{CH_3}_{Cl}$$
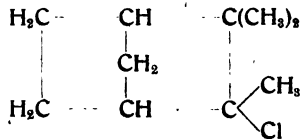
Camphene hydrochloride.

Camphene hydrochloride occurs in snow-white crystals (m. p. 125 to 127°) and shows a strong odour of menthol differing enterely from that of pinene hydrochloride or *iso*bornyl chloride. The compound splits off HCl soon after its preparation, and readily passes over into *iso*bornyl chloride, so it is stable only for a short time. Camphene hydrochloride, on shaking with water, or preferably on treatment with alkalies, is transformed nearly quantitatively into camphene hydrate.

J. Schindelmeiser[2]) reports on attempts to split off hydrogen chloride from pinene monohydrochloride by means of Reychler's reaction (with potassium phenate) with the object of obtaining camphene and camphor. Anhydrous potassium phenate (2 mol.) prepared with an excess of potassium hydroxide was mixed thoroughly with pinene hydrochloride (1 mol.) and the mixture distilled immediately. After removing the phenols the author was able to prove, in the distillate, the presence of camphene (in shape of *iso*bornyl acetate after heating with glacial acetic acid in a sealed tube; *iso*borneol, m. p. 212°; from the latter, camphene, m. p. 50°, $a_D \pm 0$) and of bornylene, besides some terpinene and diphenyl oxide (m. p. 28°, b. p. 246°). Since, however, this process allows but 25 per cent. of the pinene to be transformed into camphor, it is of no interest from a commercial standpoint. The oil of *Abies sibirica*, Ledeb. offers a more advantageous crude material, as it contains 35 to 50 per cent. of bornyl acetate. Schindelmeiser was able to split off the acetic acid readily and quantitatively by a very cheap process; the borneol obtained was successfully transformed into camphor on commercial scale by electrical processes. A Franco-Japanese company intends, as per Schindelmeiser, to obtain camphor on a large scale in Siberia from the oil of the Siberian pine.

On α- and β-pinene, from French turpentine oil, compare p. 74 of this *Report*.

Limonene. — A process for obtaining limonene and pinene nitrosochlorides, worked out years ago by K. Löffl[3]), is published by H. Rupe[4]). It gives far better yields than the usual method (with ethyl or amyl nitrite) and consists in introducing a mixture of nitrous gases and hydrogen chloride into a solution of the hydrocarbon. The gases must be mixed in the correct proportion and must react at a temperature as low as possible. If hydrogen chloride is in excess only a green oil results with but very little crystalline nitrosochloride, the amount of which otherwise reaches 90 per cent. of that calculated[5]).

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[1]) Germ. pat. appl. C. 29517, Sept. 25, 1921. — [2]) *Pharmacia* 1921, N° 1 (Reval). As per a copy kindly forwarded to us. — [3]) *Über Reduktionen in der Reihe der cyclischen Oxime und Nitrosochloride*. Dissertation, Basle 1915. — [4]) *Helvet. chim. acta* 4 (1921), 149. — [5]) According to Wallach (*Terpene und Campher*, 2nd ed., p. 69) the preparation of nitrosochlorides by Tilden's process (introducing vapours of nitroxyl chloride into the chloroform solution of the terpenes at — 10°) is troublesome. Wallach's method (treatment with amyl nitrite and concentrated hydrochloric acid), however, works quickly and satisfactorily.

The investigation of the *sesquiterpenes* by means of the usual oxidation processes, or with application of heat, has hitherto not been very satisfactory. L. Ruzicka and J. Meyer[1]) undertook to elucidate the constitution of these bodies by aid of the dehydrogenation method. For this reason, the author heated cadinene (b. p. 134 to 136° at 13 mm.) with sulphur to 200 to 265°. After repeated distillation with sodium they arrived at a naphthalene hydrocarbon $C_{15}H_{18}$ (b. p. 157 to 158° at 12 mm.; 291 to 292° at 720 mm.; $d_{40}^{19°}$ 0.9792; $n_{D19°}$ 1.5851; mol. refr. $C_{15}H_{18}/5$ calc. 64.73, found 67.78) which was transformed into the picrate $C_{21}H_{21}O_7N_3$ (m. p. 115°) and regenerated from the latter, hence was obtained in the pure state.

The hydrocarbon behaved like a fully saturated body when treated with a solution of bromine in carbon disulphide, or of potassium permanganate. On mixing with an alcoholic solution of trinitroresorcinol the hydrocarbon yielded the styphnate $C_{21}H_{21}O_8N_3$, m. p. 138°. By reduction with sodium and ethyl alcohol the authors obtained the dihydro compound $C_{15}H_{20}$ (b. p. 151 to 153° at 12 mm.) which was oxidised already by dilute permanganate solution with formation of acids and which gave no addition-product with picric acid.

The authors obtained likewise from a fraction b. p. 125 to 138° (12 mm.) containing cadinene from East Africa copaiba balsam oil by treatment with sulphur products yielding the identical picrate of the m. p. 115°. Hence other sesquiterpenes occuring in East African copaiba oil, provided they are derivatives of naphthalene, must contain the same nucleus as does cadinene.

On *tetrahydroatractylene*, vide p. 48 of this *Report*.

Concerning *machilene*, see p. 48 of this *Report*.

Alcohols.

A process invented by C. Paal[2]) for the preparation of inactive *citronellol* (dihydro-geraniol) by reducing geraniol with hydrogen in presence of palladium or platinum has been patented in Switzerland[3]).

G. Vavon and J. Detrie[4]) publish various details on the preparation of cyclo*hexanol* by hydrogenating phenol. The yield of *cyclo*hexanol differs but slightly (about two-thirds of the phenol used) even if the details of the process are varied widely. The velocity of the reaction is great; 400 g. of phenol, dissolved in 300 g. of acetic acid, added by aid of 15 g. platinum up to 100 litres of hydrogen per hour. Hydrogenation proceeded far less smoothly when the hydroxyl group was absent, or when it was linked to an alcoholic or acid radical. *Cyclo*hexanone was proved to appear as inter-mediate product and disappears again, as the reaction passes on.

Terpineol. — By heating terpin hydrate with an organic sulphonic acid, preferably with quinoline sulphonic acid, R. Marchand[5]) obtained terpineol.

On condensing citronellal with acetic anhydride R. H. Pickard, H. Hunter, W. Lewcock and H. Smith de Pennington[6]) obtained only two (and probably no more) of the four possible isomerides of iso*pulegol*, these two being *l*- and *d-α-isopulegol*. As the yield

[1]) *Helvet. chim. acta* 4 (1921), 505. — [2]) Cf. Germ. Pat. 298193, Aug. 7, 1913. — [3]) Swiss Pat. 89555, Dec. 17, 1919. As per *Chem. Zentralbl.* 1921, IV. 1323. — [4]) *Compt. rend.* 172 (1921), 1231. — [5]) Brit. Pat. 153605, Dec. 9, 1920. As per *Chem. Zentralbl.* 1921, II. 359. See also p. 141 of this *Report*. — [6]) *Journ. chem. Soc.* 117 (1920), 1248.

of the *isopulegyl* acetates rarely amounted to 50 per cent., it was probable that the aldehyde taking part in the condensation is the pure dextrorotatory compound of the formula $CH_2 : C(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CHO$ [1].

The hydrogen phthalate of the mixture of alcohols obtained from the condensation product could be separated by the fractional crystallisation of the magnesium and strychnine salts. Magnesium l-*isopulegyl* phthalate, $C_{35}H_{42}O_8Mg \cdot 6H_2O$, m. p. 111°; strychnine salt, m. p. 205°; l-*isopulegol*, b. p. 88° (10 mm.); d-α-*isopulegol* (still containing, apparently, about 10 per cent. of l-*isopulegol*), $d_{10}^{19.5°}$ 0.9172; $[α]_{D19.5°} + 29.3°$. On oxidation with chromic acid at 50°, gave *isopulegones* which gave identical lævorotatory oximes (m. p. 121°, volatile in steam) and semicarbazones (m. p. 171°). When reduced by hydrogen, the alcohols formed l- and α-*neo*menthol respectirely, both of which, when oxidised, gave l-menthone.

The authors then give extensive tables on the constants of l-*iso*pulegol and its esters with the fatty acids (C_2 to C_{14}) and graphs on the rotation of the esters as influenced by temperature and wave-length.

Menthol. — In a paper entitled, "Contributions towards the knowledge of derivatives of l-menthol" *(Zur Kenntnis der Ableitungsprodukte von l-Menthol)*, E. A. Lück[2]) reports on some preparations obtained by him from l-menthol and menthone. By heating of menthol with concentrated sulphuric acid for one hour he claims to have obtained a sesquiterpene $C_{15}H_{24}$ or $C_{30}H_{48}$ *(sic)* brownish-black, thickish mass) and furtheron, by nitration, a nitrososesquiterpene (! nitrosesquiterpene) $C_{30}H_{47}NO_2$ (decrepitating on heating). Lück prepared also a menthyl cyanide and herefrom a menthane carboxylic acid (termed by him methylene mentholic acid [*sic*]; white needles, the m. p. of which could not be kept constant [*sic*]), the corresponding aldehyde, and from the latter the secondary (!) alcohol, and a ketone.

All these bodies are enumerated with their constitutional formulæ (as Lück imagines them to be) but without the least proofs of identity, without giving the necessary constants, or any analytical results. It is desirable that the autor may supplement his work in this respect and thus elucidate its results.

Borneol. — A process has been published[3]) for the preparation of borneol from turpentine oil, consisting in treating the oil with tetrachlorophthalic acid and decomposing the resulting dibornyl ester of the acid with alcoholic caustic soda solution. A mixture of one pt. tetrachlorophthalic acid and 4 pts. turpentine oil, or crude pinene is heated for twelve hours to 106 to 108°, then for two hours to 125°, and finally for six hours to 140°. After cooling the unattacked terpenes are removed by steam or vacuum-distillation and the residue, mainly dibornyl tetrachlorophthalate, is saponified by alcoholic sodium hydroxide. The borneol, purified in the usual manner, is optically active and free from *iso*borneol. The yield amounts to 17 to 18 per cent. of the crude pinene employed. A large portion of the pinene as well as the tetrachlorophthalic acid is recovered.

If an organic solvent, such as anisole, a ketone, or an aromatic ester, is added to the mixture of pinene and acid prior to the heating, the reaction passes off more smoothly and the yield is raised up to 29 per cent.[4]).

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[1]) Cf. the paper by Prins, *Chem. Weekbl.* 14 (1917), 692; *Report* 1918, 123. — [2]) *Apotheker-Ztg.* 36 (1921), 279. — [3]) *Fabriques des produits chimiques de Thann et de Mulhouse.* Fr. Pat. 510002, Nov. 25, 1920. Brit. Pat. 144604, Dec. 3, 1919. Germ. Pat. Appl. F. 47011 published Jan. 12, 1922. — [4]) Brit. Pat. 158533, Nov. 1, 1920. (Add. Pat. to Brit. Pat. 144604.) As per *Journ. Soc. chem. Industry* 40 (1921), A. 561.

According to another process devised by L. Schmidt[1]) the bornyl and *iso*bornyl esters of organic acids are obtained in a good yield and free from by-products when these acids are heated with pinene or pinene-containing oils with an addition of boron trioxide. This latter reagent acts as a general condensing agent for pinene and organic acids by which pinene is esterified in a short time quantitatively even in open vessels. It is said to offer particular advantage to act on the mixture with boric, metaboric, or tetraboric acids on the anhydrides of the organic acids; For instance, 13.6 pts. of pinene or turpentine oil, 9 pts. of glacial acetic acid, and 1 pt. of boron trioxide are heated to its the boiling point under a reflux tube, until the ester content increases no more. The ester mixture is washed with water and fractionated *in vacuo* and yields on saponification with alcoholic potash pure borneol + *iso*borneol with a m. p. of 197 to 199°. The unchanged boron trioxide can be used again.

The process may be modified[2]) by substituting the boron trioxide by so-called mixed anhydrides of boric and of organic acids, such as boric acetic anhydride. This mixed anhydride, a simple additional product of the formula: —

$$3 \begin{array}{c} R-CO \\ R-CO \end{array} O + B_2O_3 = 2B(O \cdot CO \cdot R)_3$$
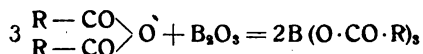
is preferably prepared in the course of the reaction. For instance, 136 kg. of pinene, 60 kg. of glacial acetic acid, 10.2 kg. of acetic anhydride, and 2.3 kg. of boron trioxide are heated together for several hours on a water-bath, the reaction-product is rinsed with water as soon as the ester-content has reached a maximum, and the acetates of borneol and *iso*borneol are obtained by fractional distillation. Saponification yields a mixture of pure borneol and *iso*borneol, m. p. 197 to 198°.

F. Martin[3]) started some experiments on the acetylation of borneol and *iso*borneol. His investigation culminated in the result that in estimating borneol or alkylborneol the alcohol must be heated for three hours with 3 parts of acetic anhydride and some sodium acetate up to 145 to 150°. With less time, or less acetic anhydride, acetylation remains incomplete, as Martin states. (The acetylation was performed in an oil bath at a temperature close to the boiling point.)

Contrary to these statements it is quite sufficient when in the quantitative acetylation of borneol, equally so of geraniol, menthol, and santalol, 10 ccm. each of the alcohol and of acetic anhydride are boiled for one hour with 2 g. of sodium acetate. Years ago[4]) we established, by way of experiment, the correctness and practicability of this method.

According to L. G. Wesson[5]), *iso*bornyl *ester* and *camphene* are obtained by heating a mixture of a carboxylic acid and of pinene hydrohalide with some zinc, the proportion of which not exceeding 5 per cent. of the pinene hydrogen halide employed.

Carvomenthol. — When reducing α-phellandrene nitrite with sodium and alcohol, Wallach and Herbig[6]) had obtained, in addition to tetrahydrocarvone (carvomenthone) and tetrahydrocarvylamine, *l*-tetrahydrocarveol (*l*-carvomenthol), but they abstained from examing the resulting alcohol for optical isomerism. V. Paolini[7]), on repeating these experiments, found that two isomeric forms of *l*-carvomenthol are generated in the

        [1]) Germ. Pat. Appl. Sch. 50927, Oct. 3, 1921. — [2]) Germ. Pat. Appl. Sch. 53704, Oct. 3, 1921. Add. to Appl. Sch. 50927. — [3]) *Journ. de Pharm. et Chim.* VII. 23 (1921), 168. — [4]) *Report* April 1910, 155. — [5]) U. S. Pat. 1372382, March 22, 1921. As per *Chem. Zentralbl.* 1921, II. 1063. — [6]) *Liebig's Annalen* 287 (1895), 378. — [7]) *Rend. della R. Accad. dei Lincei* 30 (1921), 265. As per a separate copy kindly forwarded to us.

process. The tetrahydrocarveol obtained from nitro-α-phellandrene (α-phellandrene, b. p. 75° at 15 mm.; d_{150} 0.848; α_D — 81°30'; n_{D200} 1.4769) by reduction with sodium and absolute alcohol showed the following constants: — b. p. 218° (corr.); d_{150} 0.9073; $[\alpha]_D$ — 10.83°, n_{D150} 1.463. From this alcohol the author prepared, by the cold process, the hydrogen phthalate of l-carvomenthol (m. p. 89°; $[\alpha]_D$ — 45°4') which yielded on saponification pure l-α-carvomenthol (b. p. 218° [corr.]; d_{150} 0.9074; α_D — 20.38°; n_{D150} 1.463). From the mother liquor of the carvomenthol phthalate mentioned above a second, syrupy hydrogen carvomenthol phthalate was produced, which on transformation into its silver salt (m. p. 175 to 176°) yielded furtheron l-β-carvomenthol (b. p. 218° [corr.]; d_{150} 0.9071; $[\alpha]_D$ — 8.63°; n_{D150} 1.463). Paolini proposes to term the isomeric carvomenthols obtained by him[1]) from carvone, for sake of differentiation, d-γ-carvomenthol ($[\alpha]_D$ + 1.82°) and l-γ-carvomenthol ($[\alpha]_D$ — 1.83°).

Furthermore, Paolini[2]) succeeded in obtaining from d-carvone, by following the directions given by Vavon[3]), on reduction with hydrogen and platinum, a carvomenthol, the constants of which were in accord with those of Vavon's preparation, with exception of the rotation ($[\alpha]_D$ — 2.75°, instead $[\alpha]_D$ — 24.7°). Paolini proved the products with different rotatory power to consist of mixtures of optical isomerides. Either the one or the other isomeride preponderated, according to the more or less complete process of the reduction. From carvomenthol ($[\alpha]_D$ — 2.75°) the author, by aid of his so-called cold process[1]) (viâ the di-d,β-carvomenthyl phthalate, m. p. 85°, $[\alpha]_D$ + 38.53°), was able to separate two isomeric compounds: — d,β-carvomenthol (b. p. 218° [corr.]; d_{150} 0.9074; $[\alpha]$ + 8.29°) and l,β-carvomenthol (b. p. 218° [corr.]; d_{150} 0.9073; $[\alpha]_D$ — 8.54°; n_{D150} 1.463; identical with the one of the two isomerides resulting from nitrophellandrene, see above).

Terpin hydrate. — According to a patent granted to the *Sociéte Landaise du terpinéol*[4]), terpin hydrate may be obtained from turpentine oil by means of the following contrivance: — A wooden vat, lined with lead, and filled with turpentine oil and dilute acid, is connected with two pumps of acid-resisting metal. The suction pipe of the one pump dips into the acid, that of the other into the oil, whereas the discharge pipes terminate in the oil and the acid respectively. On putting both pumps in motion a very close mixture of both acid and oil results within a short time, yielding terpin hydrate.

Terpin hydrate is, according to R. Marchand[5]), obtained in almost theoretical quantity and in the crystalline state on mixing oil of turpentine (one pt.) with a 23 per cent. sulphuric acid (2 pts.) and shaking vigorously in an atmosphere of nitrogen or carbon dioxide for about 90 hours.

Concerning the estimation of terpin hydrate, see p. 113 of this *Report*.

P. Lipp and C. Padberg[6]), with the object of studying the behaviour of apo*tricyclol* (I), a derivative of the hitherto unobtainable *cyclo*propanol (II), prepared the first-mentioned alcohol from tricyclenic acid amide (III), which, owing to the lability of the trimethylene ng was primarily degraded according to Hofmann-Jeffreys[7]) down to apotricyclyl-ethylurethane (m. p. 114 to 116°). In this reaction, tricycloyl-*apo*tricyyl-urea (decomp.

[1]) Cf. *Bericht* (Germ. ed.) 1921, 113. — [2]) *Rend. della R. Accademia dei Lincei* 30 (1921), 371. As per print kindly forwarded to us. — [3]) Cf. *Report* October 1911, 150. — [4]) Fr. Pat. 522657, Aug. 14, 1920. ۟e also *Chem. Zentralbl.* 1921, IV. 1328. — [5]) Brit. Pat. 153606, Nov. 10, 1920. As per *Journ. Soc. chem. ۟dustry* 40 (1921), A. 716. — [6]) *Berl. Berichte* 54 (1921), 1316. — [7]) *Berl. Berichte* 30 (1897), 898.
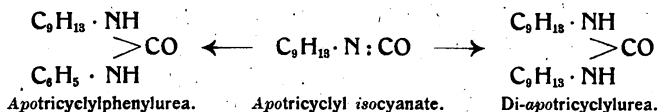
p. 238 to 239° [corr.], on slow heating) resulted as by-product, the *iso*cyanate formed in the main reaction acting with some of the unattacked amide:—
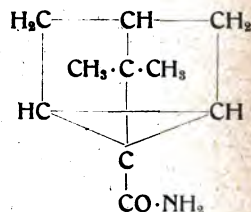
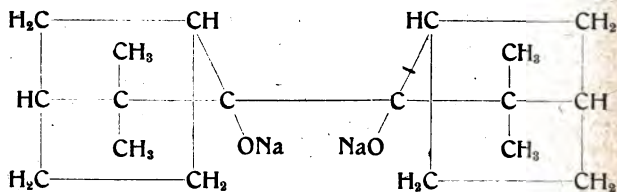$$C_9H_{13}N:C:O + H_2N\cdot CO\cdot C_9H_{13} = C_9H_{13}\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_9H_{13}.$$
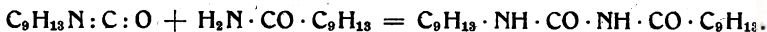
Careful saponification, performed by fusing with solid caustic potash, yielded *apo*-tricyclylamine $C_9H_{13}NH_2$, m. p. 104° (unsharp), besides camphenilone and camphenilol.

With the object to characterise the unstable *apo*tricylylamine, the authors brought the body in reaction with, *inter alia*, phosgene, obtaining thereby as primary reaction-product a liquid compound, probably *apo*tricyclyl *iso*cyanate. The latter was transformed by aniline into *apo*tricyclyl-phenyl-urea, partly also into symm. di-*apo*tricyclyl-urea:—

$$\begin{array}{ccc}
\begin{array}{l} C_9H_{13}\cdot NH \\ \qquad >CO \\ C_6H_5\cdot NH \end{array} \leftarrow C_9H_{13}\cdot N:CO \rightarrow & \begin{array}{l} C_9H_{13}\cdot NH \\ \qquad >CO \\ C_9H_{13}\cdot NH \end{array}
\end{array}$$

Apotricyclylphenylurea.   Apotricyclyl *iso*cyanate.   Di-*apo*tricyclylurea.

On diazotising the hydrochloride of *apo*tricyclylamine with sodium nitrite, *apo*-tricyclol resulted, the reaction passing off fairly well; intermediarily, a comparatively stable nitrite was formed. The alcohol *apo*tricyclol (m. p. 75 to 80° [unsharp], b. p. 82 to 86° at 12.5 mm.; phenylurethane, m. p. 121.6 to 122° [corr.]), on exposure to the air, deliquesces in the course of a few hours forming a viscid oil. When boiled with a dilute mineral acid, equally when heated (without water, by ketisation) in a current of dry hydrogen, *apo*tricyclol yields quantitatively camphenilone. With phosphorus pentachloride, *apo*tricyclol passes over into camphenilone dichloride (IV), m. p. 168 to 169°. Ethereal solutions of the alcohol, on treatment with metallic sodium, yielded, without evolution of hydrogen, the sodium compound of camphenilone pinakone (V) from which the methyl ether was obtained, dimethyl sulphate reacting quantitatively, and methyl iodide only partly.
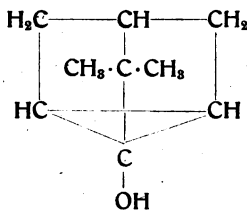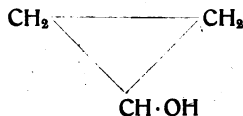
(I) Apotricyclol.   (II) Cyclopropanol.   (III) Tricyclenic acid amide.
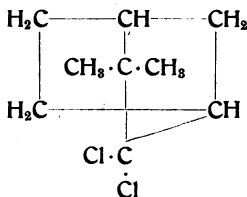
(IV) Camphenilone dichloride.   (V) Sodium compound of camphenilone pinacone.

As to optical investigations of *geraniol* and *citronellol*, vide p. 116 of this *Report*.

The publications by Fromm and Klein on *olibanol* (see p. 36 of this *Report*) and by Müller on the constitution of *reuniol* (see p. 116 of this *Report*) are discussed by H. Heller[1]).

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[1]) *Deutsche Parf.-Ztg.* 7 (1921), 22.

On a new α,β-ketonic alcohol, $C_9H_{10}O_3$, compare p. 150 of this *Report*.

From atractylol, Seisi Takagi[1]) obtained, by reduction with hydrogen and platinum in glacial acetic acid, *dihydroatractylol* $C_{15}H_{28}O$ as a viscid oil, $[\alpha]_{D120}+14.9°$.

Aldehydes.

K. W. Rosenmund and F. Zetsche[2]), by catalytic dehydrogenation by means of the "copper-quinoline-nitro-body" and of oxygen, obtained from primary aliphatic, aromatic and equally hydrocyclic alcohols the *aldehydes*, from secondary alcohols the *ketones*. Tertiary alcohols remain unaffected. The following examples are cited by the authors: — benzophenone from benzhydrol (yield, 92 per cent.), "fermentation" valeric aldehyde from "fermentation" amyl alcohol (80 per cent.), acetaldehyde from ethyl alcohol (52 per cent.), propionic aldehyde from propyl alcohol (5 per cent.), *iso*butyric aldehyde from *iso*butyl alcohol (75 per cent.), o-chlorobenzaldehyde from o-chlorobenzyl alcohol (86.2 per cent.), fural from furyl alcohol (74 per cent.). The method is particularly suited with the difficultly, or non-volatile, alcohols; with the volatile alcohols, the method offers no advantages compared with the usual processes.

The method worked out by Rosenmund and Zetsche[3]) for the catalytic preparation of aldehydes from the corresponding acid chlorides lends itself likewise to the preparation of polyaldehydes, as the authors found in community with Chr. Flütsch[4]). The following aldehydes were obtained by this method, with an average yield of 75 to 85 per cent.: — octanedial = suberic dialdehyde (di-semicarbazone, m. p. 183 to 185°; dioxime m. p. 152°); phen-dimethylal-1,3 = *iso*phthalic dialdehyde, m. p. 88 to 89°; phen-dimethylal-1,4 = *tere*phthalic dialdehyde, m. p. 116°. *Ortho*phthalic dialdehyde, however, was unobtainable from the o-phthalic acid chloride, probably the o-acid dichlorides are rearranged to the asymmetric form owing to the palladium chloride formed in the reduction.

The following process for preparing *aromatic hydroxyaldehydes* has been patented in the U. K. in favour of the Société chimique des usines du Rhône[5]): — Phenols or their derivatives are treated at suitable temperatures with formaldehyde in presence of a nitroso compound, such as nitrosobenzene, nitrosonaphthalene, or p-nitroso-dimethylaniline. If necessary, a condensating agent, e. g., hydrochloric acid, is added. When the reaction has passed off the solvent is removed by distillation and the hydroxy aldehyde worked up as usual.

The specification deals with the preparation of vanillin by starting from guajacol, formaldehyde, and p-nitrosodimethylaniline. In the same manner anisic, protocatechuic, p-hydroxybenzoic, and salicylic aldehydes are obtainable.

Closely related to this process is the method specified by H. Haakh[6]): — Phenols, or derivatives thereof, are allowed to react with formaldehyde, or bodies splitting off formaldehyde, and aromatic nitroso compounds, e. g., p-nitrosodimethyl(ethyl)aniline, p-nitrosophenol, in presence of a condensing medium (hydrochloric acid). By this method, anisic aldehyde may be prepared from anisole, and vanillin from guajacol.

[1]) *Journ. pharm. Soc. Japan* 1921, N° 473. Cf. also p. 47 of this *Report*. — [2]) *Berl. Berichte* 54 (1921), 2033. — [3]) Cf. *Report* 1918, 122. — [4]) *Berl. Berichte* 54 (1921), 2888. — [5]) Brit. Pat. 161679, April 13, 1921; cf. also French Pat. 523407, Aug. 18, 1921, and Swiss Pat. 95560, Nov. 1. 1921. — [6]) Brit. Pat. 157850, Febr. 17, 1921. As per *Chem. Zentralbl.* 1921, IV. 121.

Polymerisation of the most unstable acrolein to insoluble disacryl may be prevented, as was found by Ch. Moureu, Ch. Dufraisse, P. Robin, and J. Pougnet[1]), by adding a small amount of phenols or bodies containing such, such as pyrogallol (in proportion 1:1000), pyrocatechol or hydroquinone (1:500), gallic acid (1:250), or ethereal tannin solution (1:100). Extracts of tanning agents act in the same manner. These phenols are likewise capable of arresting the once started polymerisation of acrolein. The aldehyde, when treated with these agents, remains stable for years, provided that it is kept in the dark and at a temperature not exceeding 30°.

Citral. — E. Knoevenagel and G. Oelbermann[2]) have continued the work of the first-named author[3]) on testing the constitution of compounds of the citral series by optical methods. The values observed by the authors of the specific normal exaltation of citral were in good accord with the figures observed formerly by v. Auwers and Eisenlohr, as well as with those found by the last-named investigator for the system — C(R):CH·CHO (E ΣRefr. 1.25; E ΣDisp. 45 per cent.). Whereas a preparation of citral after keeping for 48 hours at a temperature of — 190° had suffered a slight change (the refractive index rising from 1.48786 to 1.48821), another preparation remained unchanged after the same treatment. After three months' standing in the same sealed bottles, the preparation, on optical examination, showed a strong increase in density and a decrease in the molecular refraction. Possibly, it was the case of polymerisation, or oxidation, or of both.

With *pseudo*ionone, the authors obtained values equally in good accord with those recorded by Eisenlohr for the system — C(R):CH·CH:CH·C(R):O (E ΣRefr. somewhat above 2.7; E ΣDisp. above 110 per cent.). The optical constants remained unchanged after cooling the preparation down to — 190° for 300 hours.

From *pseudo*ionone, ψ-ionone acetate was prepared according to Knoevenagel, by means of acetic anhydride with addition of sublimed ferric chloride. B. p. 145 to 146° (15 mm.). Basing on the values read off for the exaltations (E ΣRefr. + 0.29 and + 0.42; E ΣDisp. + 7 and + 8 per cent.) the authors suggest formula (I) for the acetate, although they admit that various isomerides may be present. This assumption is rendered probable by the wide b. p. range of the freshly-prepared acetate, the main part of which boiled from 118 to 150° at 11 mm. No alteration of the optical values was noticed after cooling down to — 190° during 300 hours.

For *iso*-ψ-ionone, obtained from the preceding acetate by boiling with alcoholic caustic potash (b. p. 128 to 129° at 13 mm.) the author suggest formula (II) in view of the exaltations found (E ΣRefr. + 2.22 and + 0.39; E ΣDisp. + 10 and + 14 per cent.). Cooling down to — 190°, for 300 hours, did not affect the body; however, after ten hours' standing in an open vessel the molecular refraction, by oxidation, rose from 1.49805 to 1.50311, and after 17 hours to 1.50350. The semicarbazone, m. p. 189°, was identical with a semicarbazone obtained in the same manner from ψ-ionone acetate.

By abstracting water from ψ-ionone with zinc chloride, the authors obtained two fractions of a hydrocarbon (not quite pure, b. p. 90 to 122° [12 mm.] and 135 to 145° [21 mm.]), concerning the constitution of which nothing certain could be stated from the optical data or the chemical reactions (preparation of an oxidation-product).

The optical dispersion observed with α-citrylidene acetoacetic ester was somewhat too low, since that body is easily rearranged into the β-isomeride and therefor

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[1]) Process for stabilising acrolein. Germ. Pat. Appl. M/64903, April 7, 1921. — [2]) *Journ. f. prakt. Chem.* N. F. **102** (1921), 305. — [3]) Cf. *Report* 1919, 147.

is difficultly obtainable in the pure state. In view of this circumstance and of the optical constants found by them the authors regard the formula (III) of the ester[1]), as suggested by Steinle, as the correct one.

From a citrylidene acetoacetic ester the authors prepared, *viâ* the *α-isoester*, *α-iso-ionone*. In order to make the methods of preparation agree with the optical data, Knoevenagel and Oelbermann assign to this ketone formula (IV) in lieu of formula (II) hitherto accepted which they suggest for *iso-ψ-ionone*.

When examining *β*-citrylidene acetoacetic ester, the optical constants were not found to agree with the formula propagated by Mechtersheimer[2]) which constitutes a simple, "disturbed" conjugated system. The optical data would agree best with formula (V), with cumulated double bonds, the presence of which, however, has not been proved hitherto.
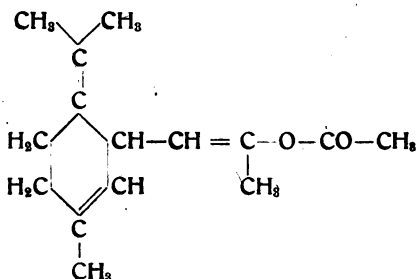
(I) *Pseudoionone acetate.*
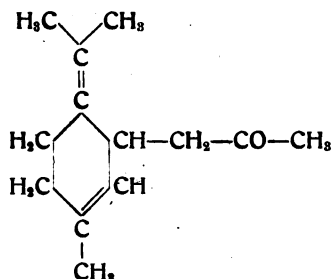
(II) Isopseudoionone.
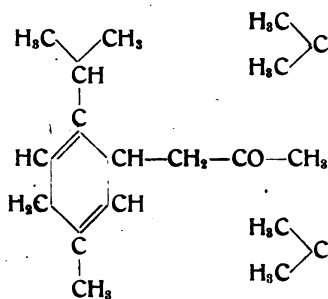
(III) α-Citrylidene acetoacetic ester.

(IV) α-Isoionone.
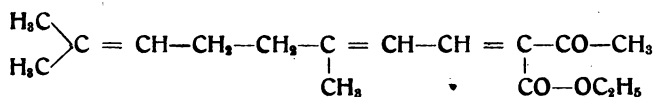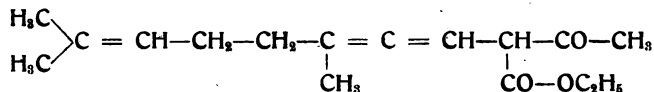
·(V) β-Citrylidene acetoacetic ester.

From the *β*-ester, a hydrocarbon was prepared according to Mechtersheimer by means of zinc chloride, which was oxidised by a mixture of nitric and sulphuric acids. The resulting body, a solid of the m. p. 154°, has not been examined further.

The formulæ for *β-ψ-ionone*, *β-isocitrylidene acetoacetic ester*, and *β-isoionone*[2]) put forward by Mechtersheimer agree approximately with the values observed by the authors.

On benzaldehyde, see p. 90 of this *Report*.

Concerning a specially devised flask for the estimation of *phenylacetaldehyde*, cf. p. 114 of this *Report*.

Salicylic aldehyde and acid are obtained, as per an American Patent 1 380 277, May 31, 1921 of J. M. Weiss and C. R. Downs[3]), by oxidising o-cresol in the vapour phase with a gas containing oxygen in the presence of a metallic oxide as catalyst.

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[1]) Cf. *Report* 1919, 148. — [2]) Cf. *Report* 1919, 149. — [3]) *Journ. Soc. chem. Ind.* 40 (1921), A. 561.

Ketones.

As to the preparation of ketones from secondary alcohols, see page 143 of the present *Report*.

In order to supplement earlier investigations[1]), P. Sabatier and B. Kubota[2]) publish new details on the catalytic reduction of *benzaldehyde* and of *aromatic ketones* by means of copper. The metal required for their experiments was prepared by slow reduction, at 200°, of black tetracupric hydrate. At 350°, benzaldehyde was reduced to benzene, toluene, and carbonic oxide. Contrary to the reduction performed formerly by aid of nickel, the carbonic oxide was not reduced to methane, but remained unchanged.

Acetophenone and ethylphenylketone were reduced catalytically by copper at 350° to ethylbenzene (b. p. 135°) and propylbenzene (b. p. 158°). Under identical conditions, benzoyl propanone was transformed into acetophenone (fairly good amount), some acetic aldehyde, ethyl alcohol, and ethylbenzene. By reducing benzoquinone over copper, at 300°, nearly exclusively hydroquinone, m. p. 169°, resulted, besides some water and phenol.

Carvone. — A. Müller[3]) was successful in preparing crystalline benzalcarvone which hitherto has been obtained by the usual condensation reactions merely as an amorphous product[4]). The condensation of carvone with benzaldehyde passed off by means of alcoholic potash lye at a temperature not exceeding $+2$ to $+3°$. The fraction b. p. 170 to 180° (10 mm.) of the reaction-product constituted the raw material for the preparation of two isomeric benzalcarvones, the residue forming the amorphous body described already by Wallach[3]). After several weeks' standing, a crystalline body separated from the viscous benzalcarvone fraction, β-benzalcarvone, m. p. 114 to 115°, $[a]_D - 815°$ ($a - 8.15°$ of a 1 per cent. alcoholic solution in a 100 mm. tube). The residual a-benzalcarvone, b. p. 191 to 193° (10 mm.); d_{150} 1.041; $[a]_D + 152.30°$, contained still a considerable amount of the β-isomeride. Neither of the isomerides (which showed red-orange and brick-yellow halochromism respectively) yielded an oxime or a semicarbazone. a-Benzalcarvone yielded an addition-product with hydrogen chloride, a dark brown oil which on heating gave off a fair amount of hydrogen chloride. On reduction with sodium both isomerides yielded benzyldihydrocarveol, the phenylurethane of which (m. p. 233 to 234°) was identical with the derivative of benzyldihydrocarveol obtained from benzaldihydrocarvone.

By means of the method founded on the absorption of ultraviolet light the author proved that on the one hand the curves for β-benzalcarvone and benzalmenthone, on the other hand those for a-benzalcarvone and benzaldihydrocarvone were, in the main identical. This behaviour shows that both β-benzalcarvone and benzalmenthone have identical structure, the former being, therefore, β-3-benzalcarvone.

How the a-isomeride is constituted remains still an open question, since benzaldihydrocarvone may exist also in a second form. As compared with carvone ($[a]_D + 59.5°$), the values for $[a]_D$ with a- and β-benzalcarvone ($+152.5°$ and $-815°$) are exceedingly high. Both isomerides demonstrate very satisfactorily that on introducing aromatic radicals into the nucleus, *i. e.*, by accumulating the double linkings, the rotation is markedly increased.

According to M. Matsui and S. Shimizu[5]), *menthone* can be reduced electrolytically in sulphuric or hydrochloric acid solution to menthol. The best results are obtained

[1]) Cf. Sabatier, *La catalyse en chimie organique*, 2nd ed., p. 190 to 196. — [2]) *Compt. rend.* 172 (1921), 733. — [3]) *Berl. Berichte* 54 (1921), 1471. — [4]) *Liebig's Annalen* 305 (1899), 274. — [5]) *Mem. Coll. Sci. Kyoto* 4 (1920), 245. As per *Journ. Soc. chem. Ind.* 40 (1921), A. 162.

when using an amalgamated tin or lead cathode, the cathode solution constisting of a mixture of 75 per cent. sulphuric acid (40 to 45 cc.) with 94 per cent. alcohol (35 to 40 cc.) at a temperature below 15°. The current used is 6 to 8 ampères per 100 sq. cm. at 11 to 13 volts. The yield of menthol is only 25 per cent., and the product was difficult to purify. An oily by-product is always obtained, which is a more highly reduced body, possibly menthane.

By reducing *thujamenthone* with hydrogen and nickel at 280°, M. Godchot[1] obtained dimethyl-1,2-*iso*propyl-3-*cyclo*pentane, a liquid of terpene-like odour with the constants:. b. p. 148 to 149°, d_{150} 0,793, n_{D150} 1.4364. The same body had been prepared years ago by Godchot and F. Taboury[2] from dihydrocamphorone. On treating thujamenthone with magnesium methyl iodide, Godchot obtained a mixture of two isomeric trimethyl-1,2,3-*iso*propyl-4-*cyclo*pentenes which on further reduction with hydrogen and nickel at 180° yielded the same body, trimethyl-1,2,3-*iso*propyl-4-*cyclo*pentane (b. p. 157 to 158°; d_{130} 0.7833; n_{D130} 1.4326), likewise with a terpene-like odour.

Additionally, the author prepared a new bicyclic ketone, dimethyl-2,3-*iso*propyl-4-*cyclo*pentylidene-dimethyl-2,3-*iso*propyl-4-*cyclo*pentanone-1, by condensing thujamenthone by means of calcium hydride[3]. This new product was a light yellow liquid with a camphoraceous odour and the constants: b. p. 182 to 184° (12 mm.); d_{150} 0.9123; n_{D150} 1.4825.

Camphor. — By acting with sodium *iso*amylate on camphor at 140°, in presence of an excess of *iso*amyl alcohol, F. Martin[4] obtained in a good yield, a mixture of alkyl derivatives of camphor and borneol ("camphol"). He then treated the reaction product, dissolved in benzene, with potassium permanganate and obtained *iso*amylcamphor (b. p. 273°; α_{D180} 59.22°[5]) [in alcoholic solution]; semicarbazone, m. p. 188°). By reducing the reaction-product of camphor and sodium *iso*amylate with sodium and absolute alcohol the author arrived at a white greasy body smelling of borneol; b. p. 190° (61 mm.); d_{40}^{00} 0.9611; α_D 16.55°[5] (in alcoholic solution), which consisted of a mixture of stereomeric bodies. On heating, for three hours, at 140° with the equal part of acetic anhydride and some sodium acetate, the body yielded acetyl*iso*amylcamphol (b. p. 169 to 170° [30 mm.]; d_{40}^{150} 0.9402; $\alpha_D + 7.42°$ [in alcoholic solution]; phenylurethane of *iso*amylcamphol, m. p. 111°).

H. Rupe and W. Diehl[6] prepared the following derivatives of *hydroxymethylene camphor:* — methylene camphor-phenylhydroxylamine (m. p. 106 to 107°), the methyl ether of this body (m. p. 75 to 76, very sensitive to light; on exposure to sunlight the compounds deliquesces to a brown mass and separates a sublimate of delicate yellow needles, m. p. 196 to 198°, probably camphor quinone, the ethyl ether of methylene camphor-phenylhydroxylamine (m. p. 162 to 164°), the *p*-nitrobenzoate of the same body (m. p. 179.5 to 180°). On reducing methylene camphor-phenylhydroxylamine, anilido-methylene camphor resulted (m. p. 165 to 167°), which was identical with the anilide obtained by Bishop, Claisen, and Sinclair[7] by condensing hydroxymethylene camphor with aniline.

By heating camphor and fural with sodamide in benzene solution, Wolff[8] arrived at *fural camphor*, m. p. 64°, easily soluble in ether, alcohol, and benzene, less soluble

[1] *Compt. rend.* 172 (1921), 686. — [2] *Bull. soc. chim.* IV. 13 (1913), 601. — [3] Cf. *Compt. rend.* 169 (1919), 62. — [4] *Journ. de Pharm. et Chim.* VII. 21 (1921), 417. As per *Bull.* Roure-Bertrand Fils, April 1921, 104. — [5] The direction of rotation is not given. — [6] *Helvet. chim. acta* 4 (1921), 388. — [7] *Liebig's Annalen* 281 (1894), 358. — [8] *Compt. rend.* 172 (1921), 1357.

in light petroleum. When trying to reduce it to furyl camphor by catalytic reduction according to Sabatier and Senderens in presence of nickel, it was completely reduced to tetrahydrofurylcamphor, b. p. 166° (14 mm.).

Following the process worked out by Haller and Bauer[1]) the author prepared, *viâ* the organomagnesium compounds: — phenylfurylcamphor $C_{10}H_{15}O \cdot CH(C_6H_5) \cdot C_4H_3O$, m. p. 114°, benzylfurylcamphor, $C_{10}H_{15}O \cdot CH(C_7H_7) \cdot C_4H_3O$ (viscid oil); *p*-tolylfurylcamphor, $C_{10}H_{15}O \cdot CH(C_6H_4 \cdot CH_3) \cdot C_4H_3O$, b. p. 234° (17 mm.); *p*-anisylfurylcamphor, $C_{10}H_{15}O \cdot CH$ $(C_6H_4 \cdot OCH_3) \cdot C_4H_3O$, b. p. 255° (17 mm.).

In a later communication, the author publishes the molecular refractions and the specific rotations of the above-mentioned compounds, which agree with the constants found formerly by Haller and Müller[2]) with the condensation-products from camphor and aldehydes. Furalcamphor shows a strong exaltation of the molecular refraction, the specific rotation, and the molecular dispersion, which is caused by the double bond linked to the furane nucleus and which disappears on reduction.

In connection with earlier work done on mono- and dialkyl derivatives of camphor[3]), A. Haller and P. Ramart[4]) communicate that the amide of dimethylcampholic acid shows the m. p. 81 to 82° and not, as stated before[5]), 72 to 73°. On reducing this amide with sodium and absolute alcohol, the authors obtained, on rectification, the nitrile of dimethyl-campholic acid $C_8H_{14} \Big\langle \begin{smallmatrix} CH(CH_3)_2 \\ CN \end{smallmatrix}$ (b. p. 131 to 133° [14 mm.], 245 to 247° [ord. press.]). On heating with sulphuric acid to 85 to 100° the nitrile again passes over into the original amide (m. p. 81 to 82°). When the nitrile was reduced with sodium and absolute alcohol, dimethylcampholamine (b. p. 123 to 124° at 20 mm.; $[\alpha]_{D25°} + 30.1°$) resulted in quantitative yield. By reducing the phenyl ester of dimethylcampholic acid (b. p. 190 to 195° at 30 mm.) — not though with the ethyl ester — with sodium and absolute alcohol, the authors obtained dimethylcampholic alcohol (b. p. 139 to 140° at 20 mm.; $[\alpha]_{D24°} + 32°$).

As to the preparation of camphor from pinene hydrochloride see p. 137 of this *Report.*

Epicamphor. — In continuation of the paper by J. Bredt and W. H. Perkin jun.[6]) which dealt with the preparation and the properties of epicamphor, Perkin jun. and A. F. Titley[7]) have prepared some derivatives of *l*-epicamphor which they compare with the analogous bodies obtained from the isomeric *d*-camphor[8]).

When *l*-epicamphor is treated with sodium and *iso*amyl formate in presence of ether, hydroxymethylene-*l*-epicamphor is formed (m. p. 89°, turning but slowly yellow and viscous; semicarbazone, m. p. 197°) to which the authors assign, in analogy to the constitution[9]) assumed for hydroxymethylene-*d*-camphor, the formula (I)
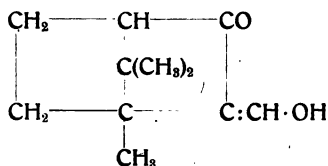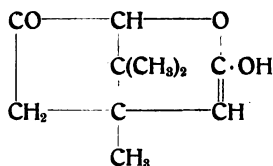
(I) Hydroxymethylene-epicamphor.   (II) Lactone of hydroxyketodihydroepicampholenic acid (tautomeric formula).

[1]) *Compt. rend.* 142 (1906), 971; 146 (1908), 717. — [2]) *Ibidem* 128 (1899), 1370. — [3]) Cf. *Report* 1919, 160. — [4]) *Compt. rend.* 178 (1921), 682. — [5]) *Report* 1919, 161. — [6]) Cf. *Report* April 1914, 140. — [7]) *Journ. chem. Soc.* 119 (1921), 1089. — [8]) *Liebig's Ann.* 281 (1894), 314; 356 (1907), 251. — *Berl. Ber.* 30 (1897), 243. — [9]) *Journ. chem. Soc.* 95 (1909), 171.

The substance gave a violet coloration when ferric chloride was added to its alcoholic solution, and exhibited mutarotation to a slight extent only, and that in an opposite sense to the mutarotation of the corresponding camphor derivative ($[\alpha]_D$ of a freshly prepared benzenic solution rose from $-125.5°$ to $-130.5°$ after 24 hours). Benzoyloxymethylene-epicamphor melted at 106°; aminomethylene-l-epicamphor, m. p. 122°, was obtained by heating hydroxymethylene-epicamphor with aqueous ammonia; it does not exhibit mutarotation, contrary to the corresponding camphor derivative. Anilinomethylene-l-epicamphor, m. p. 101°, no mutarotation; β-naphthylaminomethylene-l-epicamphor, m. p. 109 to 110°, slight mutarotation.

By heating l- or d-epicamphoroxime with sulphuric acid of 20 per cent. the authors obtained l-epicampholenonitrile (b. p. 145° [100 mm.], $[\alpha]_D - 27.4°$, passing over by hydrolysis into l-α-epicampholenic acid, b. p. 166° (30 mm.), $[\alpha]_D - 38.4°$ and d-epicampholenonitrile (b. p. 146 to 147° [100 mm.], $[\alpha]_D + 26.2°$; d-epicampholenic acid, b. p. 164 to 165° [30 mm.], $[\alpha]_D + 39.2°$).

Attempts to prepare β-epicampholenonitrile and its derivatives under the identical conditions as for obtaining β-campholenic derivatives[1]), were unsuccessful.

On reduction, l-epicampholenonitril is converted into l-epicamphylamine, b. p. 128° (100 mm.).

When l-epicampholenic acid is oxidised with potassium permanganate, the main product formed is a mixture of syrupy acids from which a ketonic acid (semicarbazone, m. p. 203°) could be isolated. In addition, there is formed the lactone of hydroxy-ketodihydroepicampholenic acid (II), m. p. 80°; $[\alpha]_D + 45.8°$. On oxidising the syrupy acids from the permanganate oxidation with chromic acid, an optically active, monobasic acid, (semicarbazone, m. p. 168°) was obtained.

Piperitone. — In their paper on the ketone piperitone contained in various eucalyptus oils, H. G. Smith and A. R. Penfold[2]) had arrived at the conclusion that piperitone is either Δ^4-menthenone-3 or Δ^1-menthenone-3. L. Givaudan & Co.[3]) were able to prove that the properties of the ketone — except in its rotatory power — answered to the Δ^1-menthenone-3 prepared originally by Wallach[4]) from a trihydroxyterpane m. p. 120°, subsequently found by us[5]) in Japanese peppermint oil and by Roberts[6]) in the oil of *Cymbopogon sennaarensis*. Hence, Givaudan & Co. regard piperitone as identical with Δ^1-menthenone-3. We wish to add that, although this conclusion does not seem to be fully proved, yet piperitone appears to be a Δ^3-menthenone. The reason for our opinion has been given in our preceding *Bericht* (Germ. ed.) p. 24, footnote.

Δ^1-Menthenone-3.
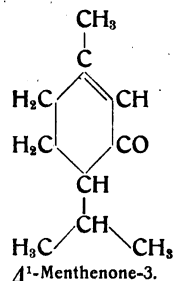
W. D. Cohen[7]) tested various alcohols as to their power of reducing *benzophenone* when exposed to sun-light. In all cases, whenever a reaction took place, benzopinacone was produced. The presence of water retarded the reaction. The reducing action was: — with methyl alcohol, 100 per cent.; *cyclo*hexanol, above 90 per cent., benzyl alcohol about 80 per cent., geraniol about 17 per cent., citronellol and cinnamyl alcohol 0 per cent. of the ketone. The alcohols were transformed respectively into formaldehyde; *cyclo*hexanone; triphenylglycol, resin, a little benzaldehyde; citral.

This reduction of aromatic ketones is a photochemical process and hence the reaction-velocity independent of the concentration of the benzophenone. The oxidation

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[1]) Cf. *Berl. Ber.* 30 (1897), 243, 405. — [2]) Cf. *Bericht* (Germ. ed.) 1921, 24. — [3]) *Perfum. Record* 12 (1921), 80. — [4]) *Liebig's Annalen* 362 (1908), 271. — [5]) *Report* October 1910, 97. — [6]) Cf. *Report* 1916, 18. — [7]) *Rec. trav. chim. Pays-Bas* 39 (1921), 243. As per *Chem. Zentralbl.* 1921, III. 785.

of the alcohols, however, being a purely chemical reaction depends in its speed on the concentration of the alcohol.

A new optically active α,β-ketonic alcohol $C_9H_{10}O_2$ composed of equal molecules of acetaldehyde and benzaldehyde and possessing the constitution $C_6H_5CO \cdot \overset{*}{C}HOH \cdot CH_8$ or $C_6H_5\overset{*}{C}HOH \cdot COCH_3$ has been obtained by C. Neuberg and J. Hirsch[1] by means of an enzymatic process. The authors proved with this synthesis, where two aldehydes unite by a fermentation process and form a ketone, that an enzyme exists capable of linking straight-lined carbon chains. This new enzyme connecting carbon with carbon, was termed "carboligase". However, a direct union of acetaldehyde and benzaldehyde by fermentation could not be effected, but it succeeded when the biological predecessor, carboxyacetaldehyde, i. e. pyruvic acid, or also sugar, was employed. The authors proceeded in the following manner: — A mixture of sugar, or pyruvic acid, yeast (or the juice of macerated yeast), and benzaldehyde was left to stand for three days and was then filtered and extracted with ether, after the fermentation had come to an end. The residue of the ether was a light yellow oil with a pungent odour reminding of benzyl alcohol (b. p. 102 to 156° at 15 mm.) which gave a strong reaction with sodium nitroprusside and which precipitated instantaneously cuprous oxide from cold Fehling's solution. 0.1 ccm. of the oil dissolved in 10 ccm. of absolute alcohol, showed a rotation of — 0.75° in a 100 mm. tube. On standing at the air, signs of decomposition, such as a smell of benzaldehyde, were noticed. The authors were unable to obtain a uniform fraction boiling within narrower limits, in spite of repeated distillation, but they were successful in preparing various derivatives of the product: — phenylhydrazone, m. p. 96°; semicarbazone, m. p. 189°; thiosemicarbazone, m. p. 204 to 205°; p-nitrophenylosazone, m. p. 264 to 265° — which served for identifying the product and as a proof for the correctness of the formulæ given above.

It could not be elucidated in which manner the fermentation of sugar or of pyro-racemic acid passes off in presence of benzaldehyde. The authors leave it open for discussion whether a specially reactive form of acetaldehyde is formed by the scission of pyroracemic acid with carboxylase, which unites with benzaldehyde, or whether the biological condensation starts already with benzaldehyde and pyroracemic acid.

Phenols and Phenol Ethers.

Carvacrol. — According to Gibbs and Phillips[2], a good yield of carvacrol is obtained from p-cymene sulphonic acid only when the process is carried on in an autoclave. With reference to this statement, A. W. Hixson and R. H. Mc.Kee[3] claim to have obtained a good yield (76 per cent.) of carvacrol from p-cymene sulphonic acid when working at ordinary pressure. The carvacrol of Gibbs and Phillips (prepared with or without pressure) is said to contain 6 to 8 per cent. of thymol, which would escape detection by the method of analysis used by Gibbs and Phillips.

D. C. L. Sherk[4] has published a thesis entitled, *Thymol and carvacrol problems,* of which we discussed some details in our last *Bericht* (Germ. ed.) 1921, p. 119. In addition to the compounds mentioned there the author prepared the alkali salts of nitrosocarvacrol and nitrosothymol by dissolving the nitrosophenols in the theoretical

[1] *Biochem. Ztschr.* 115 (1921), 282. As per a special copy kindly forwarded to us. — [2] Cf. *Bericht* (Germ. ed.) 1920, 147. — [3] *Journ. ind. eng. Chem.* 12 (1920), 296. — [4] Thesis (Fritzsche Bros. Fellow), Madison, Wis., 1920. From a copy kindly forwarded to us.

quantity of 2N-alkali made up free from carbonate, and evaporating to dryness in a vacuum desiccator. The salts were coloured red or blue, corresponding either to the nitroso or to the *iso*nitroso (oximido) type. The silver salt of nitrosocarvacrol was at first greenish-brown, turning later to olive and finally brown.

For identifying both phenols, the benzoyl derivatives of the nitroso compounds are particularly useful: — benzoyl nitrosothymol, (from alcohol, m. p. 109 to 110.5°; no oxime obtainable); benzoyl nitrosocarvacrol (from alcohol, m. p. 85 to 87°; oxime, obtained by treatment with hydroxylamine hydrochloride and sodium bicarbonate; m. p. from benzene, 156 to 157° with evolution of gas). Alkali transforms the oxime into nitroso*thymol*.

By treating the alkali salts of both nitrosophenols with methyl iodide in alcoholic solution, the author obtained nitrosocarvacrol methyl ether (m. p. 39°) and nitrosothymol methyl ether (liquid).

Isosafrole. — S. Nagai[1]) reports on the various geometrical isomerides of *iso*safrole, on which Hoering and Baum[2]) had published a paper some time ago. When safrole is rearranged to *iso*safrole, the stable *trans*-form is obtained best by heating 1 pt. safrole, 0.5 pt. potassium hydroxide, and 1 pt. 98 per cent. alcohol up to 94 to 95° for four to five hours. The labile *cis*-form, which on heating passes over into the other isomeride, is formed when using less alkali and more alcohol and at a lower temperature. The author describes the following preparations: — c *(cis)-iso*safrole (b. p. 242 to 243°; d_{40}^{15} 1.1162 to 1.1168; n_{D15° 1.5630 to 1.5632; picrate, m. p. 68.5°); t *(trans)-iso*safrole (b p. 247 to 248°; d_{40}^{15} 1.1230 to 1.1235; n_{D15° 1.5730 to 1.5736; picrate, m. p. 73.5 to 74°). The dibromides of both isomerides differ merely by the angle of rotation: — *cis*-dibromide, $[\alpha]_{D20^\circ}$ + 13.35°, *trans*-dibromide, $[\alpha]_{D20^\circ}$ + 4.45°.

By distilling *in vacuo* or by heating with potassium hydroxide, the *t*-dibromide yielded the *c*-monobromide (b. p. 168 [19 mm.]), and *vice versâ*, the *c*-dibromide gave the *t*-monobromide (b. p. 154° [19 mm.]) of *iso*safrole. *cis*-Isosafrole monobromide as well as *t*-dibromide, when heated to 70°, readily split off hydrogen bromide with formation of piperonyl allylene $CH_2O_2 : C_6H_8 \cdot C : C \cdot CH_8$ (m. p. 41 to 42°, b. p. 249 to 251°). On the other hand, *t*-monobromide and *c*-dibromide yielded piperonyl allylene only when heated to 150° and with an excess of alkali.

On heating the monobromides with zinc and alcohol, the author obtained the corresponding *iso*safroles. This reaction furnishes a method of obtaining, from *c-iso*safrole, *via* the bromine compounds, *trans*-derivatives, and again leads back to the initial body.

By oxidising both isomerides with potassium permanganate or ozone, the same body, piperonal, resulted.

A new method for the preparation of the *alkamines* of anethole, *iso*safrole, and methyl*iso*eugenol has been published by J. Takeda and S. Kuroda[3]). The *pseudo*-ureas of these bodies, obtained from their dibromides with urea, are constituted, in the opinion of the authors, as demonstrated by the annexed formula, and on treatment with acetic anhydride and sodium acetate they yield the acetyl derivatives and the acetylated oxazolidones. These bodies are broken up, on boiling with alkali, more readily than the ψ-ureas and lend themselves, therefore, preferably for the preparation of the alkamines. Following this method, the authors arrived at the following derivatives: — anethole alkamine

$$R \cdot CH\text{———}NH$$
$$\big|\qquad\qquad \big\rangle C : NH$$
$$R' \cdot CH\text{——}O$$
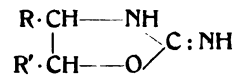
[1]) *Journ. Coll. Engin.*, Tokyo 11 (1921), 83. From a special reprint kindly forwarded to us. — [2]) *Journ. pharm. Soc. of Japan* 1921, No. 467. As per *Chem. Zentralbl.* 1921, I. 789.
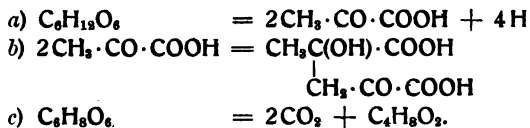
$CH_3O \cdot C_6H_4 \cdot CH(NH_2) \cdot CH(OH) \cdot CH_3$ (m. p. of the acetyl derivative, 111 to 112°), *iso*-safrole alkamine $CH_2O_2 : C_6H_3 \cdot CH(NH_2) \cdot CH(OH) \cdot CH_3$ (m. p. 79°), hydrochloride (m. p. 210 to 215°), N-acetyl*iso*safrole alkamine (m. p. 156°), N-benzoyl*iso*safrole alkamine (m. p. 139°), N-dimethyl*iso*safrole alkamine (m. p. 171 to 173°), methyl*iso*eugenol alkamine $(CH_3O)_2 :$ $C_6H_3 : CH(NH_2) \cdot CH(OH) \cdot CH_3$ (m. p. 95 to 96°), hydrochloride (m. p. 222°), N-benzoate (m. p. 140°), N-methylate (m. p. 90 to 91°).
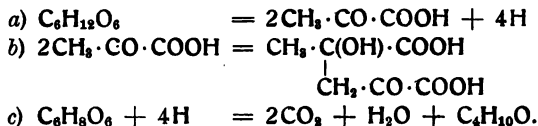
Acids, Esters, and Lactones.

Although the *butyric acid fermentation process* of the carbohydrates has been investigated extensively and has been explained by assuming a condensation process like that of acetaldol, or crotonaldehyde, the experimental ground for this theory was still missing. The process was slucidated only by the investigations of C. Neuberg and his collaborators. Since Neuberg and Nord[1] had shown that in bacterial degradation in the sugar series, just as in the alcoholic fermentation of sugar by means of yeast, acetaldehyde is formed, Neuberg and B. Arinstein[2] were now able to perform successfully their investigations on the character of the butyric acid and the butylic alcohol fermentations. Their experiments proved that when starch syrup is fermented by *Bacillus butylicus*, Fitz in presence of calcium carbonate, peptone and a solution of nutrient salts, 25.16 per cent. butyric acid, 7.20 per cent. acetic acid, 1.7 per cent. butylic alcohol, and 2.23 per cent. ethyl alcohol are the result. If under the same conditions di-sodium sulphite is added, with the object to "catch off" and eliminate the intermediarily-formed acetaldehyde, the result runs as follows: — 0 per cent. butyric acid, 20.35 per cent. acetic acid, 0 per cent. butylic alcohol, 13.47 per cent. ethyl alcohol, and 7.61 per cent. acetaldehyde; acetic acid and ethyl alcohol may be regarded as dismutation-products of acetaldehyde. These results prove that the formation of acetaldehyde depends in a certain manner on the true saccharogenic butyric fermentation process. The authors found also that α-keto-γ-valerolactone-γ-carboxylic acid, the so-called aldol of pyroracemic acid (see below under b), on fermentation with *Bac. butylicus*, yields butyric acid in addition to some acetic acid. Pyroracemic acid being considered as the intermediary stage of acetaldehyde[3], it may be assumed that the degradation process of sugar, on butyric fermentation, passes off with pyroracemic acid as intermediate body, this acid being condensed to the aldol and the latter split up to butyric acid.

In the authors' opinion, both processes, that of the butyric acid fermentation and of the butylalcoholic fission of sugar, can be expressed by the following rough formulæ:—

Butyric acid fermentation of sugar:

a) $C_6H_{12}O_6$ $= 2CH_3 \cdot CO \cdot COOH + 4H$

b) $2CH_3 \cdot CO \cdot COOH = CH_3C(OH) \cdot COOH$
$| \atop CH_3 \cdot CO \cdot COOH$

c) $C_6H_8O_6$ $= 2CO_2 + C_4H_8O_2$.

Butylic alcohol fission of sugar:

a) $C_6H_{12}O_6$ $= 2CH_3 \cdot CO \cdot COOH + 4H$

b) $2CH_3 \cdot CO \cdot COOH = CH_3 \cdot C(OH) \cdot COOH$
$| \atop CH_2 \cdot CO \cdot COOH$

c) $C_6H_8O_6 + 4H$ $= 2CO_2 + H_2O + C_4H_{10}O$.

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[1] *Biochem. Ztschr.* 96 (1919), 133. Cf. *Bericht* (Germ. ed.) 1920, 140. — [2] *Biochem. Ztschr.* 117 (1921) 269. As per a special reprint kindly forwarded to us. — [3] Cf. p. 150 of this *Report*.

Finally the authors were successful in proving a fact of importance from a biological stand-point, that when dextrose is fermented with a pure culture of *Bac. butylicus*, Fitz, caproic acid and higher fatty acids resembling caprylic and caprinic acids are formed.

Of the four *pinononic acids* obtained from different primary bodies, the acid obtained by Kerschbaum on oxidising verbenol from verbena oil was known to be identical with the acid prepared by Blumann and Zeitschel[1] from the autoxidation products of pinene (verbenol and verbenone). E. Fromm and R. Klein[2] now established the identity of these two acids with the degradation-product obtained by Fromm and Autin[3] from olibanol (of frankincense oil). Kerschbaum's pinononic acid semicarbazone (from verbenone), when mixed with the semicarbazone of the acid from olibanol, showed no depression of the melting point. In order to test the behaviour of the fourth specimen of the acid, which had been obtained by Wagner and Ershtchikovski[4] by oxidising pinene with permanganate, Fromm and Klein oxidised pure pinene (b. p. 156 to 158°; d_{180} 0.8683), from French turpentine oil, with permanganate according to the directions given. However, instead of the pinononic acid as expected they obtained a pinononic acid contaminated by a small quantity of an acid of the m. p. 100°. They are, therefore, of opinion that the acid obtained by Wagner and Ershtchikovski is due to some impurity in their pinene, preferably to the autoxidation-products containing verbenol and verbenone. For the reason of clearing up this question the authors started some experiments on olibanol, without, however, arriving at the result desired. (Cf. also p. 36 of this *Report*.)

An extensive publication by O. Aschan on *pinabietinic acid*, which we dealt with[5] following an abstract from the Swedish, has now appeared in *Liebig's Annalen*[6]. The crude material serving for the preparation of the acid was a pine oil called in Sweden *Tallolja*. This pine oil results on evaporating the "black lye" *(Schwarzlauge)* of the manufacture of sulphate cellulose and treating the soap obtained therefrom with sulphuric acid or acid sodium sulphate. The product is a dark, thick oil, soluble in sodium carbonate, which by distillation with superheated steam can be separated into readily and difficultly volatile fatty and resinous acids. It was from such a distillate that Aschan obtained pinabietinic acid.

By catalytic hydrogenation with hydrogen in xylene solution, K. W. Rosenmund and F. Heise[7] obtained from *benzyl benzoate* and *benzhydryl benzoate* benzoic acid (94 per cent.) and hydrocarbons. If increasing quantities of quinoline were added (0.2 to 1 mgr. to 5 gr. of the ester) the ester saponification was gradually checked. With toluene as solvent the reaction did not take place.

Benzaldehyde, when treated in the same manner in xylene solution, yielded benzyl alcohol (8 per cent.) and preferably dibenzyl ether (52 per cent.). On addition of quinoline in rising quantities, the proportion of the ether formed decreased in favour of the alcohol.

From *benzyl alcohol* and the corresponding acid chlorides H. A. Shonle and P. Q. Row[8] prepared the following *esters:* — Benzyl laurate (m. p. 8.5°, b. p. 209 to 211° [11 mm.], d_{250}^{250} 0.9457, n_{240} 1.4812), benzyl myristate (m. p. 20.5°, b. p. 229 to 231°

[1] Cf. *Report* October 1913, 103. — [2] *Liebig's Annalen* 425 (1921), 208. — [3] Cf. *Report* April 1914, 63. — [4] Cf. *Berl. Berichte* 29 (1896), 881. — [5] Cf. *Bericht* (Germ. ed.) 1920, 149. — [6] *Liebig's Annalen* 424 (1921), 117. — [7] *Berl. Berichte* 54 (1921), 2038. — [8] *Journ. Americ. chem. Soc.* 43 (1921), 361.

[11 mm.], $d_{25^\circ}^{25^\circ}$ 0,9321, n_{240}.14803), benzyl palmitate (m. p. 36.0°, $d_{25^\circ}^{38^\circ}$ 0.9136, n_{500} 1.4689), benzyl stearate (m. p. 45.8°; $n_{25^\circ}^{50^\circ}$ 0.9075, n_{500} 1.4663), benzyl oleate (liquid at 0°, b. p. 237° [7 mm.], $d_{25^\circ}^{25^\circ}$ 0.9330, n_{250} 1.4875).

For the production of large amounts of these benzyl esters it is recommended to allow benzyl chloride to react with the anhydrous alkali salt of the fatty acid dissolved in an excess of that acid.

From by-products resulting from the hydrolysis of proteins S. Kodama[1]) a series of mostly odoriferous esters: — *ethyl α-acetoxyisohexoate*, b. p. 120 to 121°/20 mm., the corresponding *methyl* ester, b. p. 99 to 100°/20 mm.; *ethyl α-benzoylisohexoate*, b. p. 174 to 176°/17 mm.; *ethyl α-isovalerylisohexoate*, b. p. 125 to 128°/10 mm.; *ethyl* and *amyl α-chloroisohexoates*, b. p. 152 to 153°/10 mm. and 113 to 114°/8 to 10 mm.[2]). These two esters can be converted into the corresponding esters of *iso*hexoic acid by reduction with sodium amalgam. α-Acetoxy*iso*hexoic acid phenyliminochloride forms prisms which when treated with acetic ester and magnesium yield α-ethoxy*iso*hexaldéhyde as an oil.

Bergaptene. — As a continuation of their earlier endeavour[3]) to obtain bergaptene and xanthotoxin synthetically, P. Karrer, A. Rüdlinger, A. Glattfelder, and L. Waitz[4]) were successful in confirming the constitution suggested for the 2-methyl-5-hydroxy-coumarone-4-acrylic acid described formerly. It remained, therefore, still unanswered why the coumarone ring prevents the closing of the coumarin ring. The authors now regard the formula suggested by Thoms[3]) for bergaptene as uncertain. With the purpose of elucidating this question the authors undertook to arrive at bergaptene from phloroglucinol monomethyl ether *via* methoxy-7-acetoxycoumarin. Unfortunately it was impossible to add bromine to the double bond of the coumarin ring without simultaneous bromination of the nucleus, so that the experiment had to be broken off.

Glucosides.

R. H. Clark and K. B. Gillie[5]) determined the *salicin* content in the bark of various British Columbian willows and poplars. The bark was dried for 48 hours at a temperature of about 110° and digested for three hours with boiling water. The proteins were removed by adding lead acetate and the filtrate treated with emulsin. When hydrolysis had passed off the amount of the glucose formed was estimated with Fehling's solution. The salicin content of the various barks proved to vary considerably; in the most cases the spring barks gave higher values than the corresponding autumn barks.

Species	Average salicin content	
	autumn samples	spring
Salix Nuttallii[6])	3.90 per cent.	4.49 per cent.
Salix Hookeriana	9.81 „ „	5.09 „ „
Salix sitchensis	2.80 „ „	7.38 „ „
Salix lasiandra	2.50 „ „	2.51 „ „
Salix purpurea	—	3.83 „ „
Populus trichocarpa	0.955 „ „	3.86 „ „
Populus tremuloides	3.77 „ „	2.45 „ „

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[1]) *Journ. Tokyo chem. Soc.* 41 (1920), 965. As per *Journ. chem. Soc.* 120 (1921), I. 220. — [2]) Evidently, there is here some mistake concerning the boiling points. — [3]) Cf. *Bericht* (Germ. ed.) 1921, 123. — [4]) *Helv. chim. acta* 4 (1921), 718. — [5]) *Americ. Journ. Pharm.* 93 (1921), 618. — [6]) This species is not recorded in the *Index Kewensis* of 1910.